

ADSORPTION OF PHOSPHATE AND AMMONIUM IONS ON CLAY MINERALS

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In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY**

**by
SHRIPAD B. SHELDARKAR**

**to the
DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
JULY, 1979**

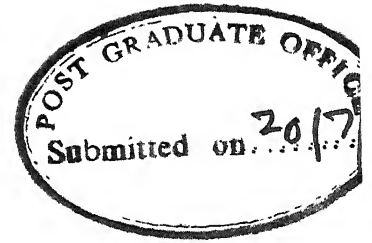
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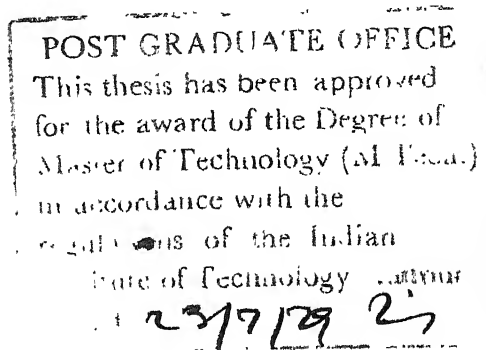


CERTIFICATE

Certified that the work presented in this thesis entitled 'Adsorption of Phosphate and Ammonium Ions on Clay Minerals' by Shri Shripad B. Sheldarkar has been carried out under my supervision and it has not been submitted elsewhere for a degree.

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July, 1979



ADSORPTION OF PHOSPHATE AND AMMONIUM IONS
ON CLAY MINERALS

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A study of the literature revealed that very little work has been done regarding the understanding of basic mechanisms of adsorption of common pollutants onto clay minerals. The objective of this work was, therefore, to study the basic process of adsorption of two common ions viz. NH_4^+ and PO_4^{3-} onto three selected clay minerals, viz. bentonite, kaolinite and bauxite, in agitated nonflow systems. Identifying a potential coagulant aid from these minerals was also aimed at.

Stable Na^+ -clay suspensions were prepared and used for adsorption studies. The kinetic studies revealed that the adsorption proceeds in two distinct phases. An initial rapid adsorption phase of about two hours duration accounting for 65% to 70% of the total adsorption followed by slow adsorption phase was observed. The adsorption of NH_4^+ was observed to be higher at higher pH values and higher concentrations and that for PO_4^{3-} was observed to be lower at higher pH values and lower concentrations. Intraparticle diffusion was observed to be the rate limiting step in the first phases of all the systems and the second phases of NH_4^+ -bentonite and NH_4^+ kaolinite systems. For the second adsorption phase of NH_4^+ -bauxite and all the

PO_4^{3-} -clay systems considered, a complex mechanism rather than one seems to be operative with interparticle diffusion as dominating rate limiting step. Desorption studies revealed that the fraction of NH_4^+ adsorbed over and above the cation exchange capacity is not entirely desorbable.

The adsorption isotherms did not fit into any of the conventional models, viz. Langmuir, Freundlich and BET, but closely resembled the isotherms for ionic detergents alumina systems. The mineral series for favourable NH_4^+ adsorption was Bentonite > Bauxite > Kaolinite and that for favourable PO_4^{3-} adsorption was Kaolinite > Bauxite > Bentonite. X-ray diffraction powder data conclusively established entry of PO_4^{3-} ions in the intralattice structure but was inconclusive with regard to entry of NH_4^+ ions in the intralattice structure.

Bauxite was found to have better adsorption capacity with regard to NH_4^+ and PO_4^{3-} adsorption. This was further confirmed in jar tests wherein it was found to adsorb 31.82 mg/g of NH_4^+ from 100 mg/l as N of NH_4Cl solution in tap water. Alum doses for phosphate-rich solutions were found to be exorbitantly high. In a mixed system simulating secondary effluent with common NH_4^+ and PO_4^{3-} concentrations, it was observed that NH_4^+ removal by bauxite is further improved whereas the presence of other competing ions inhibits the phosphate adsorption. Though bauxite imparts light reddish brown colour to the water, almost complete colour removal was observed on filtration through Whatman-42 filter paper and as such this colour is not expected to pose any problems after filtration.

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It has been a teamwork.

The author, not out of modesty, but out of sincere appreciation and gratitude credits the entire work to ____, and acknowledges with sincere thanks the ____

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The author fully owns any drawbacks and shortcomings in this work.

(Shripad B. Sheldarkar)

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1. INTRODUCTION

Phosphorous and nitrogen compounds are important pollutants of surface waters and are constituents of wastewater. The principal sources of ammonia nitrogen and phosphorous in wastewaters are excreta of humans and animals. Carbon, nitrogen and phosphorous are of great sanitary significance as they are the essential nutrients for growth and synthesis of aquatic flora and fauna. Monitoring the concentrations of the compounds of these elements in a water body is therefore essential to engineer either favourable growth and synthesis of the desirable aquatic flora and fauna (as in biological treatment units) or curbing of the growth of undesirable algal blooms; the object of monitoring ^{being} dependent upon what the system demands. Because of algal growth in water bodies, presence of ammonia-N and PO_4^{3-} beyond a certain concentration is undesirable. The important treatment processes for their removal are air stripping, filtration through multimedia filter beds, distillation, floatation, foam fractionation, freezing, various biological treatments, adsorption and land application.

A review of the available literature shows that a lot of work has been done on the removal of these nutrients from mixed solution systems. Most of the treatment processes are very expensive. It was felt that if a study of removal of soluble ammonia and phosphates (from condensed phosphates) by

clay minerals is undertaken the results of the study could be successfully used for designing suitable systems for land application as well as for developing a suitable coagulant aid which in addition to reducing the coagulant doses, would remove appreciable quantities of nutrients from the systems at a comparatively lower cost.

2. THEORETICAL BACKGROUND AND LITERATURE REVIEW

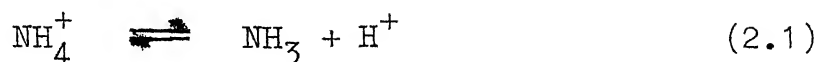
2.1 General:

The compounds of nitrogen and phosphorus are of great interest to sanitary engineers because of their importance in the life processes of the plant and animal kingdom. Of the various forms of nitrogen, compounds of more significance to sanitary engineers are NH_3 , N_2 , N_2O_3 and N_2O_5 , are the acid anhydrides of nitrous and nitric acids. Atmosphere serves as a reservoir from which nitrogen is constantly removed by the action of electrical discharge, nitrogen fixing bacteria and algae. Animals and human beings are incapable of utilizing nitrogen from the atmosphere or from inorganic compounds to produce proteins. They are dependent on plants and other animals that feed on plants to provide protein. As a result, nitrogen and phosphorous compounds are released in the waste products of the body. Domestic waste is rich in nitrogen and phosphorous compounds. Prior to the development of synthetic detergents, the origin of most of the inorganic phosphorous was the human excreta, as urine, wherein due to metabolic breakdown of proteins and elimination of the liberated phosphates in the kidneys, phosphate concentrations are high. Many of the synthetic detergents contain over 50% of polyphosphates. As a result of wide use of synthetic detergents, the inorganic phosphorous content has considerably

increased in wastewaters. The organisms involved in biological processes of sewage and industrial wastewater treatment require carbon, nitrogen and phosphorous for their survival and reproduction. Domestic sewage normally contains amounts of these nutrients in excess of that required for stabilizing the organic matter present. Deficiencies, if any, should be made up by either suitably blending wastes from two sources (e.g. domestic or industrial) judiciously or by externally adding the deficient nutrient in suitable form. Nitrogen and phosphorous are essential for the growth of algae. Such growth is often stimulated to undesirable extent in bodies of water that receive sewage or treatment plant effluents, because of nitrogen, phosphorous and other nutrients present in the sewage and as such it is necessary to see that the concentrations of those nutrients is well within the limits in the wastewater to be disposed so as to curb growth of algae in undesirable proportions.

2.2 Chemistry of Ammonia Nitrogen:

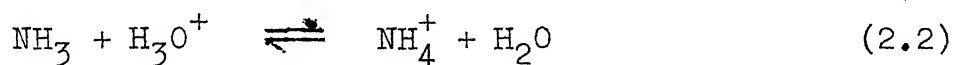
All nitrogen that exists as ammonium ion NH_4^+ in equilibrium as



is considered to be ammonia nitrogen. Under aerobic conditions, the NH_4^+ present is oxidized to nitrites by autotrophic nitrifying bacteria (Nitrosomonas) and the nitrites are further oxidized

to nitrates by Nitrobactor group. In anaerobic condition denitrification occurs all the way from nitrates form to ammonia. During denitrification most of the nitrogen in the system escapes in the form of N_2 or N_2O gas.

The solubility of ammonia is very high. One volume of water can dissolve as much as 670 volumes of the gas [Loehr (1973)]. Undissociated ammonia exists in equilibrium with the ammonium ion, in the form



The hydrogen ion concentration governs the relative quantities of these ions in a system. The ratio of undissociated ammonia divided by total ammonia concentration 'F' which in other words is the fraction of ammonia nitrogen in the undissociated form is given by

$$F = \frac{[NH_3]}{\text{Total ammonia concentration}} = \frac{10^{pH}}{10^{pH} + \frac{K_b}{K_w}} \quad (2.3)$$

where K_w and K_b are the dissociation constants for water and ammonia respectively. Loehr (1973) has tabulated values of F at various pH values and temperatures. The values of this ratio increase with increasing temperatures and pH values at 25°C, the values of F at pH values of 7 and 11 are 0.005 and 0.982 respectively. This corresponds to a free ammonia of 0.5% and 98.2% respectively. Only free ammonia is available for desorption and hence unit~~A~~ eliminating ammonia from the

system by air stripping, it is necessary to raise the pH in the basic pH range.

2.3 Chemistry of Orthophosphates and Polyphosphates:

Inorganic compounds of phosphorous of relevance to sanitary engineering practice are the orthophosphates and their molecularly dehydrated forms referred to as polyphosphates. All the polyphosphates gradually hydrolyse in aqueous solutions and revert to the ortho form from which they are derived. The rate of reversion is a function of temperature. The process is also accelerated by lowering the pH [Sawyer, and McCarty (1967); Standard Methods (1974)]. The hydrogen ion concentration governs the degree of ionization and the form(s) in which the phosphates are present in a system, e.g. at pH = 7, the predominant species are HPO_4^{2-} and H_2PO_4^- whereas at pH = 10, HPO_4^{2-} predominates with traces of PO_4^{3-} whereas at pH = 4, the predominant ion is H_2PO_4^- with insignificant amounts of H_3PO_4 [Wayman (1963)].

2.4 Removal Methods:

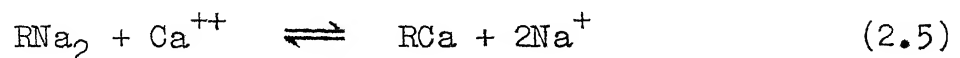
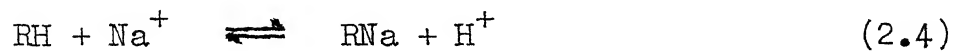
Need for removal of nutrients from wastewaters and surface waters has been emphasised in the previous section. Percent removals of these nutrients in various physicochemical and biological processes are summarized in Table 14.2 by Metcalf and Eddy (1974). The authors have further described

unit operations such as air stripping of ammonia, filtration with multimediuim filter, beds, distillation, floatation, foam fractionation, freezing, gas phase separation, reverse osmosis, chemical precipitation, ion exchange by resins, sorption onto activated alumina and land application. As the object of the present study is to study the adsorption of ammonium and phosphate ions onto some selected clay minerals so that the results of the study may be further used for designing systems for land applications and/or for applications as coagulant aids, further discussion is confined to topics related to the above areas only.

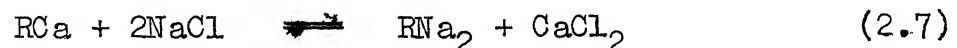
2.5 Ion Exchange:

Ion exchange is unit process by which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. The chemistry of ion exchange may be represented by the following equations.

Reaction

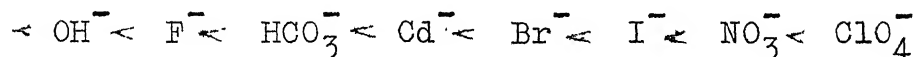
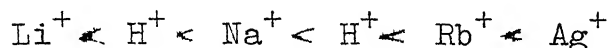


Regeneration



where R represents the resin.

For synthetic cationic and anionic exchange resins, typical ion preference series are [Metcalf and Eddy (1978)].



At low concentrations, selectivity for exchange of monovalent ion by divalent ions is in general larger than the exchange of monovalent ions by monovalent ions. However, the above series is not universally applicable for all the systems as some adsorbents have selective affinity for particular ions.

2.6 Adsorbents:

Most commonly used adsorbent used in this unit operation is activated carbon. Of late indigenous materials, such as activated char, activated rice husk, activated crushed coconut shell powder etc. have been tried [Dave (1974)]. Prohibitive cost of activated carbon has diverted the attention of investigators towards low-cost materials and amongst these soil forming clay minerals are a natural choice.

2.7 Clay Minerals:

Clay minerals are primarily hydrated silicates of aluminium or magnesium in which unit layers are arranged in stacks. There are two broad classes of the clays:

- (1) Two layered silicates (e.g. kaolinite, bauxite, etc.)
- (2) Three layered silicates (e.g. montmorillonite).

This classification is based on the linking of two fundamental structural units: (1) The silica sheet or the tetrahedral layer in which each silicon atom is surrounded by four oxygen atoms in a tetrahedral coordination, (2) Gibbsite (or brucite) sheet or the octahedral layer in which six oxygen or hydroxyl atoms surround one aluminium or magnesium atom in an octahedral coordination [Grim (1953)].

The oxygen atoms in both the tetrahedral and octahedral layers are linked in a hexagonal array. The dimensions are such that these layers can be superimposed in two or three layer packets with the oxygen atoms at the tips of the tetrahedra jointly shared by the atoms in the octahedral layer.

In the kaolinite structure, a single tetrahedral layer and a single octahedral layer are combined with a common layer of tetrahedral and octahedral atoms. The unshared oxygen atoms in the octahedral layers form OH groups. The units are continuous in the 'a' and 'b' crystallographic directions and stacked one above the other in the 'c' (vertical) direction. The unit layer (2 layer tetrahedral-octahedral group) is 5 atom thick and the repeat distance in 'c' direction is 7.38 \AA .

The montmorillonite structure is composed of units made up of two silica tetrahedral sheets with central alumina

octahedral sheet, sandwiched between the silica sheets. The combination is such that the tips of the tetrahedra of each silica sheet form a common layer. Atoms common to both the tetrahedral and octahedral layers become 'O' instead of 'OH'. The layers are continuous in the 'a' and 'b' directions and are stacked one above the other in the 'c' direction. In the stacking of silica-alumina-silica units, oxygen containing layers of each unit are adjacent to oxygen containing layers of the neighbouring units with the consequence that there is a weak bond and excellent cleavage between them. Water and other polar molecules can enter the unit layers causing the lattice to expand. The minimum repeat distance in the 'c' direction for montmorillonite is 9.6 \AA , when no polar molecules are present in the interlayer but, when, because of the presence of exchangeable cations and polar molecules like water enter the lattice, the 'c' spacing is usually of the order of 15 \AA . The basal spacing is variable due to interlayer swelling.

2.8 Origin of Surface Charge in Clays:

There are three mechanisms believed to be responsible for charge phenomenon on clay mineral surfaces. They are:

- (a) Isomorphous substitution: Substitution within the lattice structure of trivalent aluminium for quadrivalent silicon in the tetrahedral sheet and of ions of lower valency like Mg^{++} for Al^{+++} in the octahedral layer result in unbalanced charges in the structural unit of clay minerals.

- (b) Broken bonds: Broken bonds along crystalline edges of clay particles parallel to the 'c' axis would also give rise to unsatisfied charges. Bonds may be broken either in the tetrahedral or octahedral layer.
- (c) Lattice defects: Recent hypothesis for origin of charge especially for kaolinite, is a mechanism creating negative charges from lattice defects [Hunter and Alexander (1963)]. The charge is attributed to an interlayer between Si and Al layers and the postulated coordination of Al with oxygen in tetrahedral rather than octahedral arrangement.

2.9 Ion Exchange by Clay Minerals:

Clay minerals are known to adsorb certain cations and anions and retaining them in exchangeable state.

- (a) Cation exchange: In case of kaolinite and bauxite, the cation exchange is mostly due to broken bonds around the edges of silica-alumina units. Isomorphous substitution also contributes towards the C.E.C. of these minerals. In case of montmorillonite, 80% of C.E.C. is due to isomorphous substitution in the lattice structure and 20% is due to broken bonds. The unbalanced charges are satisfied by exchangeable cations present mostly on basal cleavage surface of the clay mineral and also on the edges.
- (b) Anion exchange: Van Olphen (1964) has proposed a dual charge on clay in terms of the electrical double layer

theory. Clay minerals are amphoteric in nature possessing both cation and ~~anion~~ sites for exchange, owing to presence of both positive and negative broken bonds at the crystal edges.

At low pH values, some OH^- ions ionize away from the surface leaving a positively charged site available for anion exchange. At high pH values these OH^- groups remain firmly attached to the surface and only the cations ionize away from the surface to expose negative sites. Anion exchange in montmorillonite does not take place on basal plane surfaces.

There is a controversy about whether phosphate removal by kaolinite is a surface phenomenon or the reaction takes place on basal plane by replacing OH^- ions in the lattice structure.

2.10 A Brief Review of Relevant Work Done:

2.10.1 Ammonia Removal:

Several workers have reported ammonia removal efficiencies of more than 90% in air stripping [Slecha and Culp (1967); Rao and Prasad (1971); Folkman and Wachs (1973)]. However, the air stripping towers soon get encrusted and require repeated clearing, besides having to maintain a very high pH. Nitrogen removal by ion exchange was reported by several workers. An ammonium selective cation exchanger clinoptilolite was used for ammonia removal in AWT plant,

North Verginia, to bring down the ammonium concentration to 1 mg/l [Suhr and Kepple (1975)]. The use of clinoptilolite was studied by several workers and they reported 90-96% ammonia removal [Mercer et al. (1970); Koon and Kaafman (1975); Jorgson et al. (1976)]. However, regeneration and fouling of the clinoptilolite is a problem. Stasiuk et al. (1974) studied break point chlorination to remove ammonia from secondary effluents. They found that the ammonia removal efficiency depended upon pH and ammonium to chloride ratio. Barker et al. (1975) have studied the leaching of nitrates, sulphates and phosphates in surface waters. Day et al. (1972) found that nitrates accumulated to a level of 137 mg/l in Ap horizon and 38 mg/l in C-horizon when soil is irrigated with wastewater treatment plant effluent as against 65 mg/l on Ap horizon and 12 mg/l in C-horizon when the same soil was irrigated with well water. This, according to them was due to conversion of ammonia and organic nitrogen to nitrates by microbial degradation in the soil environment. Lance et al. (1972) concluded that nitrogen was not removed from secondary sewage effluents when soil columns were flooded with wastewater for shorter intervals but almost all the ammonia and organic-N was transformed to nitrate form. With larger flooding periods, they observed nearly 30% net reduction.

2.10.2 Phosphorous Removal:

The data by Day et al. (1972) indicate that there is a considerable increase in phosphate levels in soils when the same is irrigated with wastewater effluent. Sawhney (1977) showed that phosphate in wastewater percolating through soil column is readily adsorbed by soil. However after break-through, increasingly larger concentrations of phosphates were observed leaching out into the effluent. Chen et al. (1973) have done kinetic studies of phosphate adsorption onto alumina and kaolinite. They concluded that the phosphate adsorption was higher with higher percentages of iron oxides in alumina. Many researchers have worked on adsorption/desorption of phosphate-local river sediment systems. They are, McCallister and Logan (1978); Edzwald et al. (1976); Kuo and Lotre (1974); Lee et al. (1972); Shukla et al. (1971); William et al. (1971); Green et al. (1978); Syers et al. (1973); Wall and Wilding (1976). They all observed that the composite suspended sediments generally contained more total 'P' than the quantity of P retained when adsorption maxima is reached. This is a result of P enrichment of sediment because of selective erosion and therefore exposure of clay as well as adsorption of soluble P by sediment during transport.

2.10.3 Coagulant Aids:

Coagulant aids are generally used as a remedy for effective coagulation, precisely, flocculation problems when

(a) small and slow settling flocks predominate, fragile flocks that are fragmented and sheared under hydraulic forces occur and (b) when it is difficult to achieve clarification due to interfering substances. The coagulant aids are generally used as oxidants, adsorbents or weighting agents. Activated silica and polyelectrolytes are some of the popular coagulant aids. Though the role of clays as coagulant aid in remedying some of the flocculation problems listed above has been studied, removal of soluble inorganics somehow has not been thought of.

In summary it can be stated that though removal of NH_4^+ and PO_4^{3-} ions in mixed systems of heterogeneous adsorbents (i.e. soils containing number of minerals) and wastewaters and surface waters containing number of competing ions in agitated nonflow and column systems has been done, very little work has been done on pure systems. Practically no work or data is available on the mechanism of adsorption onto clay minerals. This information is important from the point of view of effective use of low-cost clay minerals for the removal of the plant nutrients under study. As for the role of clay minerals as coagulant aids, removal of soluble inorganic impurities by these coagulant aids when coagulation is practised for the removal of these pollutants has been given practically no consideration by the research workers so far.

3. SCOPE OF INVESTIGATIONS

From the literature review, it may be seen that very little work has been done for understanding the basic mechanisms of adsorption of common pollutants onto clay minerals. It was felt that though the natural clay mineral and the common ion systems involve soils containing number of minerals and water, number of ions, studies in pure systems involving no interference from competing ions other than the one under consideration, would lead to better understanding of the mechanisms involved and would finally give useful clues for selection of type of soils rich with the type of mineral(s) found suitable both for subsequent land application and/or as potential coagulant aids. For this purpose three minerals were chosen. They were

- 1) Bentonite
- 2) Kaolinite
- and 3) Bauxite.

Bentonite is a mineral containing predominantly Montmorillonite - a three layered silicate mineral with high cation exchange capacity.

Kaolinite is a two layered silicate mineral with low cation exchange capacity. Because of the low cation exchange capacity, it is believed to have high potential for anion exchange.

Bauxite is a mineral predominantly containing oxides of Aluminium and traces of iron oxides in the form of minerals like Gibbsite. Presence of oxides of iron is supposed to have an effect on the cation exchange as well as anion exchange capacity of the minerals. The ions chosen for adsorption studies were

- 1) Ammonium ion - NH_4^+ from NH_4Cl as solute in distilled water.
- 2) Phosphate ion - PO_4^{3-} from Sodium Tripolyphosphate (STPP).

The work was proposed to be conducted in three phases.

3.1 Phase I:

It was planned to conduct necessary tests for finding out physical and chemical properties of the minerals such as specific gravity, average grain size, average surface area, cation exchange capacity, pH etc. A comprehensive table indicating all these characteristics is shown in Chapter 5.

3.2 Phase II:

Batch studies were proposed to be conducted for finding out:

- 1) The adsorption kinetics of NH_4^+ -clay and PO_4^{3-} -clay systems.
- 2) The nature of adsorption.
- 3) The possible rate limiting step in adsorption.
- 4) The adsorption isotherms at three different pH values and the ultimate adsorptive capacities. The proposed pH values for NH_4^+ -clay systems were 7, 5, and 3 and for PO_4^{3-} -clay systems were 10, 7, and 4.

5) The optimum pH for maximum removal of NH_4^+ and PO_4^{3-} ions.

3.3 Phase III:

Standard jar tests were proposed to be conducted for ascertaining feasibility of use of these clay minerals as coagulant aids.

3.3.1 Jar Tests - Set A:

Optimum pH values and concentrations obtained from Phase II studies were proposed to be used in standard jar tests in pure systems with alum as a representative coagulant. This was proposed to be done to have a meaningful correlation between Phase II and Phase III studies.

3.3.2 Jar Tests - Set B:

Identical concentrations of the solute and sorbent in tap water were proposed to be tested in standard jar tests. Effect of presence of alkalinity and other competing ion could be quantified in this phase.

3.3.3 Jar Test - Set C:

Based on the results of Phase I, Phase II and Jar Tests A and B, it was proposed to test the feasibility of using the most promising mineral at the optimum pH and concentration as a coagulant aid in a simulated secondary effluent.

The simulation was proposed to be done by taking 10% raw domestic sewage filtered through bandage cloth and diluting it with tap water. Common NH_4^+ and PO_4^{3-} concentration obtained from literature were proposed to be added to this. The optimum alum dose, reduction in optimum alum dose and the optimum contact time between the coagulant aid and the simulated secondary effluent containing both NH_4^+ and PO_4^{3-} ions in the common concentrations chosen from literature, along with organics was proposed to be evaluated in this phase.

4. MATERIALS AND METHODS

4.1 Materials:

4.1.1 Minerals:

The minerals used in this study were supplied by Cosmas Industries, Varanasi, India. The minerals are:

- 1) Bentonite
- 2) Kaolinite
- 3) Bauxite.

The minerals were sieved through 45 μ m sieve, oven-dried at 105°C for 24 hours and ground in a ball-mill for obtaining finer sizes. Clay suspensions were prepared as described in Section 4.2.1.6.

4.1.2 Sorbates:

Sorbates used were:

- 1) Ammonium chloride - analytical grade
- 2) Sodium tripolyphosphate (STPP)

The STPP was supplied by Indian Rare Earths Ltd., Udyogmandal, Kerala. Subsequent analysis showed that the sodium tripolyphosphate has:

- 1) Total phosphate = 57.5% by weight
- 2) Total phosphorus = 18.76% by weight
- 3) $\frac{\text{Ortho phosphate}}{\text{Total phosphate}}$ ratio = 0.435

4.1.3 Coagulent Used:

Alum $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$ - analytical grade was used as coagulant.

4.2 Methods:

4.2.1 Experimental methods and analytical techniques for determination of physical and chemical properties of clays and for preparation of clay suspensions.

4.2.1.1 Determination of specific gravity: Specific gravities of the minerals were calculated by specific gravity bottle method as per [Alamsingh (1974)]

Sp. gravity =

$$\frac{\text{Weight of sample in the specific gravity bottle}}{(\text{Weight of sample}) - (\text{Weight of sample} - \text{Weight of distilled water replacing the sample})}$$

4.2.1.2 Determination of average particle diameter: Clay suspensions were oven-dried and the dried samples were again pulverized to finer sizes by using a pestle and mortar. The samples were then tested in a laboratory sub-sieve sizer. One cubic cm. of each sample was placed in the sample holder. A controlled stream of air is passed through the sample. The resistance to air flow is inversely proportional to the voids and consequently to the average particle size. This resistance to flow of air is transmitted directly into the average particle diameter in μm on the dial.

4.2.1.3 Determination of soil pH: The measurement of soil pH was done as suggested by Black et al. (1954). Ten per cent clay suspension was thoroughly stirred and its surface pH was measured by a pH-meter. However, the bulk pH differs from the pH observed near the surface and the two are correlated as follows.

$$\text{pH near the surface} = \text{pH}_{\text{bulk}} - 0.89 \quad [\text{Black et al. (1954)}]$$

4.2.1.4 Determination of cation exchange capacity: Cation exchange capacity or the base exchange capacity was found out as per the Indian Standards method (I.S. 2720 - Part XXII, 1967). Base exchange is a physicochemical process wherein one type of ions (cations) adsorbed on soil particles are replaced by other type of cations. The base exchange capacity signifies the capacity of soil to retain bases upto its highest limit or it can also be defined as the power of the soil to combine with the bases in such a manner that they cannot be easily removed by leaching with water, but can be exchanged by an equivalent amount of other bases.

Ten grammes each of the Na^+ -clay samples were placed in Bachner funnels in which were put Whatman-2 filter paper discs neatly sealed with parafin wax from all the sides. The samples were then slowly leached with 500 ml of 0.2 N potassium acetate solution in 100 ml lots without any suction. This was followed by washing with distilled water and 60% alcohol. The K-soil samples were then leached by 500 ml of

1 N ammonium acetate solution in 100 ml lots. The filtrate was evaporated to dryness, redissolved in distilled water and titrated against 0.1 N HCl for the potassium acetate released with bromothymol blue as indicator. The cation exchange capacities are reported in meq/100 g units.

4.2.1.5 Determination of surface area: Elaborate surface area calculations need the chemical analysis data yielding the exact chemical composition of the mineral [Olphen (1963)]. In the absence of this data an approximate method of surface area calculations was adopted. This method [Olphen (1963)] involves approximation of the clay particle size as a thin cylinder with the diameter as found out from the sub-sieve sizer. Though crude, this method gives a fairly good idea about the magnitude of the surface area (expressed in m^2/g) of the minerals. An illustrative calculation and results are included in the next Chapter.

4.2.1.6 Preparation of clay suspensions: Clay particle by definition should measure $2\ \mu\text{m}$ or less. To separate this fraction from the minerals ground in ball mill, the minerals were suspended in a vertical cylinder for 12 hours. The supernatant liquid contained very fine particles which are likely to cause interference in subsequent analysis owing to their very fine size. They were discarded, so also were the coarser sediments like quartz etc. at the bottom. The remaining supernatant was oven-dried at 105°C . Preliminary

studies showed that exchangeable ions in the minerals like Ca^{2+} , Mg^{2+} etc. caused considerable interference in the subsequent colourimetric analysis and hence it was decided that the mineral suspensions be converted to suspensions with minerals having only one type of exchangeable cation, viz. Na^+ . This was done in two stages as suggested by Olphen (1963).

(a) Preparation of stable clay suspensions: The clay was suspended in distilled water by rigorous stirring for about 10 minutes at sufficiently high speed so as to keep the particles in suspension. The clay concentration was kept as high as possible commensurate with the capability of the stirrer to keep it in suspension. Then the suspension was diluted sufficiently to ensure gravity settling. As usually is the case all the clay samples were found to be contaminated with sufficient amounts of electrolytes and therefore there was flocculation and rapid settlement of the minerals. The clear fluid was siphoned off and the clay was again redispersed in distilled water by stirring. This procedure was repeated till the electrolyte concentrations were lowered below the flocculation value and the clay fraction stayed in suspension owing to peptization. Peptization is the process of stabilization of clay suspensions by the reversal of the positive edge charge into a negative one. (It may be noted that excess concentrations of peptizing agents on the contrary promote flocculation). At this stage particles still settling rapidly were discarded

as they formed impurities such as quartz etc. with diameters exceeding 2 μm .

(b) Preparation of Na^+ -clay suspensions: A 2 N sodium chloride solution was added to this suspension. This resulted in rapid flocculation and settlement of the clay. The supernatant fluid containing exchanged cations like Ca^{2+} and Mg^{2+} was discarded. This was repeated sufficient number of times to ensure complete ion exchange. This was confirmed by absence of these ions (viz. Ca^{2+} and Mg^{2+}) from the supernatant fluid in subsequent repetitions. Then the Na^+ -clay thus formed was washed free of residual electrolyte by repeated washings. Washings were stopped when the conductivity of the supernatant fluid was observed to be constant on subsequent washing. Initially the settlement was observed to be rapid owing to the presence of NaCl in amounts far exceeding the flocculation value. But as the suspension slowly started getting peptized, centrifugation was resorted to for separating the clay particles from the solution. The Na^+ -clay suspensions thus prepared were stored in aspirator bottles and they did stay stable over a period of a couple of months. By putting a mark on the aspirator bottles, corrections for evaporation losses were applied from time to time.

4.2.1.7 Identification of minerals and mineral impurities by X-ray diffraction: Mineral identification was done on XRD-5

diffractometer with copper target and K- α filter. X-ray diffraction takes place from lattice planes with indices (hkl) according to the Bragg's law [Brown (1961)].

$$n\lambda = 2d(hkl) \sin \theta$$

and

$$d(hkl)/n = \frac{d}{2\sin \theta}$$

where $d(hkl)$ is the true lattice spacing for planes (hkl), the wave-length, θ the glancing angle of reflection and n the order of reflection.

The samples were mounted on perspex sample holders and were scanned through $2\theta = 5^\circ$ to $2\theta = 60^\circ$ at $2^\circ/\text{min}$. The 'd' values in \AA units for all the prominent peaks in this range were found out from X-ray powder diffraction data. Intensities of the peaks were also tabulated. These tables were compared with standard data from samples with known composition from Brown (1961). Clay minerals, especially the ones under study, have basic 'd' spacing values associated with them, e.g. two layered clays like kaolinite have d-spacings in the range 7.1 to 7.2 \AA and three layered clays like montmorillonite have d spacings of at least 9.2 \AA . X-ray data for bentonite sample showed two intense montmorillonite peaks at 4.325 \AA and 2.563 \AA . It also displayed peaks characteristic of quartz, feldspars (i.e. orthoclase and plagioclase) and calcite. Approximate estimates in the bentonite samples of

the percentages by weight of montmorillonite, feldspar, calcite, quartz and rest are 70%, 20%, 5%, 4% and 1% respectively.

X-ray data for kaolinite sample showed two intense peaks at 9.92 \AA and 3.57 \AA . It also indicated traces of illite and quartz. The approximate composition being 90% kaolinite, 5% illite and 5% quartz and rest of impurities.

X-ray data for bauxite showed two intense peaks for bauxite at 4.978 \AA and 4.48 \AA . It also showed traces of gibbsite, kaolinite and quartz. The approximate composition is 70% bauxite, 20% gibbsite, 5% kaolinite and 5% quartz and rest the impurities. A comprehensive table showing physical and chemical properties of the minerals is enclosed in Chapter 5.

4.3 Analytical Techniques and Experimental Procedures in Adsorption Studies:

4.3.1 Batch Studies:

4.3.1.1 Preparation of glassware: All the glassware was thoroughly washed with chromic acid and rinsed with distilled water. The glassware was equilibrated with the corresponding concentrations of sorbates by putting on a rotatory shaker at the rate of 52 r.p.m. for 24 hours before every run. Before starting every run, the 250 ml reagent bottles thus equilibrated were rinsed with distilled water several times to ensure that no free residual sorbate is left. In addition to this precaution, blanks were taken in each run, which however, did

not show any appreciable adsorption of sorbates because the bottles were already equilibrated with the sorbates.

4.3.1.2 Procedure: In each of the 250 ml reagent bottles, 200 ml of the desired concentration of the sorbate was filled with the desired concentration of the Na^+ -minerals which were added in the form of suspensions of known concentrations. It was observed that if oven dried samples of Na^+ -clays were weighed and added, the cake however finely pulverized with pestle and mortar, took certain time to break up in the natural 2 μm size. This resulted in a deceptive adsorption kinetics in the initial stages where especially the uptake is very rapid. Hence it was decided to add the Na^+ -clays from the suspensions only.

For kinetic studies, duplicate samples with identical sorbate and sorbent concentrations were taken and the volume of sample taken out from one was made up from the other. This was done to minimise discrepancies involved in reduction in volume of the fluid in the reagent bottles. The samples were diluted suitably and centrifuged at 10,000 r.p.m. for 10 minutes. The supernatant was analysed for residual concentrations of the solutes. The equilibrium time was decided upon from the kinetic studies. Batch studies for adsorption isotherms at desired pH were conducted for the equilibrium time observed in the kinetic run. The solute concentration was the same in all the reagent bottles but the sorbent concentration varied gradually in the desired range.

4.3.2 Jar Tests:

Standard jar tests were conducted to assess the feasibility of using the minerals as coagulant aids. The coagulant used was alum $\text{Al}_2 (\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$. The test consisted of 1 minute of flash mixing at the rate of 100 r.p.m., followed by 20 minutes flocculation at the rate of 20 r.p.m. and 30 minutes of settling time. Samples collected after the 30 minutes settling time were analysed for pH, residual turbidity and residual sorbate concentrations after suitable dilutions and centrifugation at the rate of 10,000 r.p.m. for 10 minutes.

4.3.3 Determination of Ammonia Nitrogen:

Determination of ammonia nitrogen was made as per direct nesslerization method in Standard Methods (1974). The dissolved impurities are precipitated out with ZnSO_4 and NaOH at pH 10.5 and the supernatant is chelated against reprecipitation and interference of residual concentrations of dissolved impurities by the Rochelle salt solution. This sample reacts with nessler reagent producing a graduated series of yellow to brown colours.

The calibration curve was prepared by taking suitable dilutions of standard ammonium chloride solution with concentration ^{of} 10 mg/l as 'N', and on treatment with nessler reagent the absorbance readings were noted at wave-length of 420 nm.

4.3.4 Determination of Orthophosphates and Total Phosphates:

Phosphate determination was done by using a combination of the total phosphate and polyphosphate method in Standard Methods (1974) and the modified method of Tausky and Shorr as given by Warton and McCarty (1972).

The polyphosphates were hydrolyzed to orthophosphate form by boiling with strong acid solution for 30 minutes in an autoclave at 15-20 psi. The colourimetric analysis was done by the modified Tausky and Shorr method.

Inorganic phosphate reacts with ammonium molybdate under acidic conditions to form phosphomolybdic acid. This is reduced to phosphomolybdous acid by ferrous sulphate. Phosphomolybdous thus formed has an intense blue colour with adsorption maxima at 660 nm.

Reagents

- (1) Colour reagent: 4 ml of 10% ammonium molybdate in 10 N H_2SO_4 added to 36 ml of distilled water in which 2 g of FeSO_4 was added. This reagent was prepared fresh every time.
- (2) Standard phosphate solution: 143.16 mg of KH_2PO_4 was dissolved in 1000 ml of distilled water, giving a solution of 100 mg/l as PO_4^{3-} . The standards used in the calibration chart were prepared from suitable dilutions of this stock solution in the range of 10 $\mu\text{g/ml}$ to 200 $\mu\text{g/ml}$.

- (3) Trichloroacetic acid solution: 10% TCA solution was prepared by dissolving 10 gm TCA in 100 ml of distilled water.

Procedure

To 1 ml of hydrolyzed sample, 1 ml of 10% TCA was added. After thorough mixing, 1 ml of colour reagent was added and allowed to stand for 10 minutes, for colour development. The volume was made upto 5 ml and the optical density was measured at 660 nm against a reagent blank.

4.4 Instruments:

The various instruments used during the work are listed below. Common laboratory instruments are not included in the list.

1. pH meter: Expanded pH meter, 331, Systronics, 89-92. 7
2. Turbidity meter: Hach Turbidimeter, Model 2100, Hach Chemical Company.
3. Spectrophotometer Spectra-950: Neotronics Corporation, P.O. Box 7776, Bombay 400080.
4. Centrifuge: S-S-3 automatic superspeed centrifuge, Ivan Sorval Inc., U.S.A.
5. Fisher Sub-sieve Sizer: Fisher Scientific & Company, U.S.A.
6. XR DC-5 X-ray Diffractometer: General Electric Company, Wisconsin, U.S.A.
7. Jar Test Apparatus: Phipps & Bird Inc., Richmond, Virginia.

5. RESULTS AND DISCUSSIONS

This study was conducted in three different phases. The objectives of these phases of study are enlisted in Chapter 3 and the materials and methods used are described in Chapter 4. The results obtained in these phases of study are presented and discussed separately.

5.1 Phase I Studies:

In this phase, various tests were conducted and techniques for analytical calculations were adopted for finding out physical and chemical properties of the minerals, such as specific gravity, average grain size, average surface area, cation exchange capacity and pH etc. These results are given in Table I. Some of the analytical techniques and experimental procedures, which it is felt deserve more elaboration, are discussed below.

5.1.1 Calculation of Surface Area of Clay Minerals:

In the absence of elaborate chemical analysis data for exact chemical composition of the clay minerals, an approximate analytical technique was adopted as suggested by Van Olphen (1963). Though somewhat crude, this method gives a fairly good idea about the magnitude of surface area of the minerals.

Table I

Physical and Chemical Properties of Clay Minerals

Clay mineral	Physical properties				Chemical properties		
	Specific gravity	Average particle diameter μm	Surface area m^2/g	Characteristic basal spacing (from literature)	Approximate composition from X-ray diffraction results	pH	
						Surface	Cation exchange capacity meq/100 g
Bentonite	2.58	2.5	425.61	15 \AA	Montmorillonite 70% Felspar 20% Calcite 5% Quartz and rest 5%	9.00	9.89 45
Kaolinite	2.03	1.5	131.91	7.15 \AA	Kaolinite 90% Illite 5% Quartz and rest 5%	8.37	9.26 6
Bauxite	2.37	5.0	56.52	14 \AA to 15 \AA	Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) 70% Gibbsite 20% Kaolinite 5% Quartz and rest 5%	7.95	8.84 38

The values of the lattice thicknesses are taken from Brown (1961). For the average concentrations of clay-minerals used, parallel stacking arrangement of 10 unit layers are assumed to form an individual particle. A comparison of the calculated values of surface area with the common values cited in literature show that these assumptions are reasonably correct. The mineral particles are idealized as flat cylindrical plates with the diameters as found out from the sub-sieve sizer and thickness calculated from the assumed lattice arrangement. The relevant values are shown in Table II.

Table II
Physical Dimensions of Clay Minerals

Clay mineral	Average particle diameter μm	Unit layer thickness \AA	Number of units assumed in the parallel stacking arrangement	Specific gravity
Bentonite	2.5	10 \AA units @ 20 \AA c/c	10	2.584
Kaolinite	1.5	7.15	10	2.034
Bauxite	5.0	15	10	2.370

A sample calculation for bentonite is given below.

Bentonite is a three layered mineral with 10 \AA unit layers at 20 \AA c/c. The intralattice area therefore

is available for exchange for dipolar molecules like water and also for exchangeable ions with ionic diameters less than 10 \AA . The ionic diameter for NH_4^+ and PO_4^{3-} ions is 2.86 \AA and 6.00 \AA respectively [Nicholhas (1975)]. Thus in surface area calculations, the intralattice area also has been taken into consideration.

(a) External surface area calculations:

$$\begin{aligned}\text{Thickness of one particle 'h'} &= [n(n-1)(10+10) + 10] \text{ \AA} \\ &= 9 \times 20 + 10 = 190 \text{ \AA} \\ &= 1.9 \times 10^{-6} \text{ cm}\end{aligned}$$

$$\begin{aligned}\text{Volume of each particle} &= \pi r^2 'h' \\ &= \pi \left(\frac{2.5}{2} \times 10^{-4}\right)^2 (1.9 \times 10^{-6}) \\ &= 9.326 \times 10^{-14} \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{External surface area} &= 2\pi r^2 + 2\pi r h - (10-1) \times 10 \\ &= 2\pi (1.25 \times 10^{-4})^2 + 1.25 \times 10^{-10} \\ &= 14.216 \times 10^{-8} \text{ sq.cm/particle}\end{aligned}$$

$$\text{Density} = 2.58 \text{ g/cm}^3 \text{ or specific volume} = 0.387 \text{ cm}^3/\text{g}$$

$$\text{Number of particles/g} = \frac{0.387}{9.326 \times 10^{-14}} = 4.149 \times 10^{12}$$

$$\begin{aligned}\text{External surface area/g} &= (4.149 \times 10^{12})(14.216 \times 10^{-8}) \\ &= 58.985 \times 10^4 \text{ sq cm/g} \\ &= 58.985 \text{ sq m/g}\end{aligned}$$

(b) Intralayer surface area calculations:

$$\begin{aligned}
 \text{Intralayer surface area/particle} &= 18 \pi r^2 \\
 &= 18 \pi \left(\frac{2.5}{2} \times 10^{-4}\right)^2 \\
 &= 88.357 \times 10^{-8} \text{ sq cm/particle}
 \end{aligned}$$

$$\begin{aligned}
 \text{Intralayer surface area/g} &= (88.357 \times 10^{-8})(4.149 \times 10^{12}) \\
 &= 366.622 \times 10^4 \text{ sq cm/g} \\
 &= 366.622 \text{ sq m/g}
 \end{aligned}$$

$$\text{Total surface area/g} = 58.985 + 366.622 = 425.607 \text{ sq m/g}$$

Calculations for the other two minerals have been done on the same lines. However kaolinite and bentonite being two layered minerals, the external surface area equals the total surface area in both the cases.

5.1.2 X-Ray Diffraction Studies:

X-ray diffraction studies were conducted on untreated samples, samples which had adsorbed NH_4^+ or PO_4^{3-} to their full adsorptive capacities and samples that had undergone desorption till equilibrium was reached. In all the cases it was observed that the characteristic peak of quartz at $2\theta = 26.3^\circ$ showed no shift but considerably diminished intensities compared to those indicated by untreated samples indicating quantitative reduction in quartz content in the adsorbed and desorbed samples. Larger and heavier quartz particles are bound to be separated during

the process of preparation of clay mineral suspensions as explained in Section 4.2.1.6 and hence the above observation about reduction in quartz contents. NH_4^+ -clay and PO_4^{3-} -clay systems are discussed separately.

5.1.2.1 NH_4^+ -clay samples: In the case of all the three minerals, the intense peaks representing the respective minerals showed a slight shift in the 2θ values on the higher side consequently reducing 'd' values slightly. A marked reduction in intensities of these peaks also was observed. The above phenomenon was more marked in the case of bentonite samples.

(a) NH_4^+ -Bentonite samples: As can be seen from Figure 5.1, characteristic intense montmorillite peaks are seen at 4.52 \AA and 2.56 \AA in the untreated samples. These peaks are shifted to 4.35 \AA and 2.53 \AA respectively in the NH_4^+ adsorbed sample and to 4.39 \AA and 2.52 \AA respectively in NH_4^+ desorbed samples. This is seen to be associated with a marked decrease in the intensities, which suggest masking of the particles by adsorbed NH_4^+ layers along the surface. The existing data is not sufficient to comment unhesitatingly about the possibility of entrance of NH_4^+ ions in the crystal lattice though the shift in the basal (d) values suggests this. For confirming this, X-ray diffraction (powder) data with different targets should have been obtained which could not be done due to busy schedule of usage of the diffractometer. Desorbed samples indicated partial desorption from the surface coating of NH_4^+ only. The above observation equally apply to all the minerals appearing as impurities except quartz.

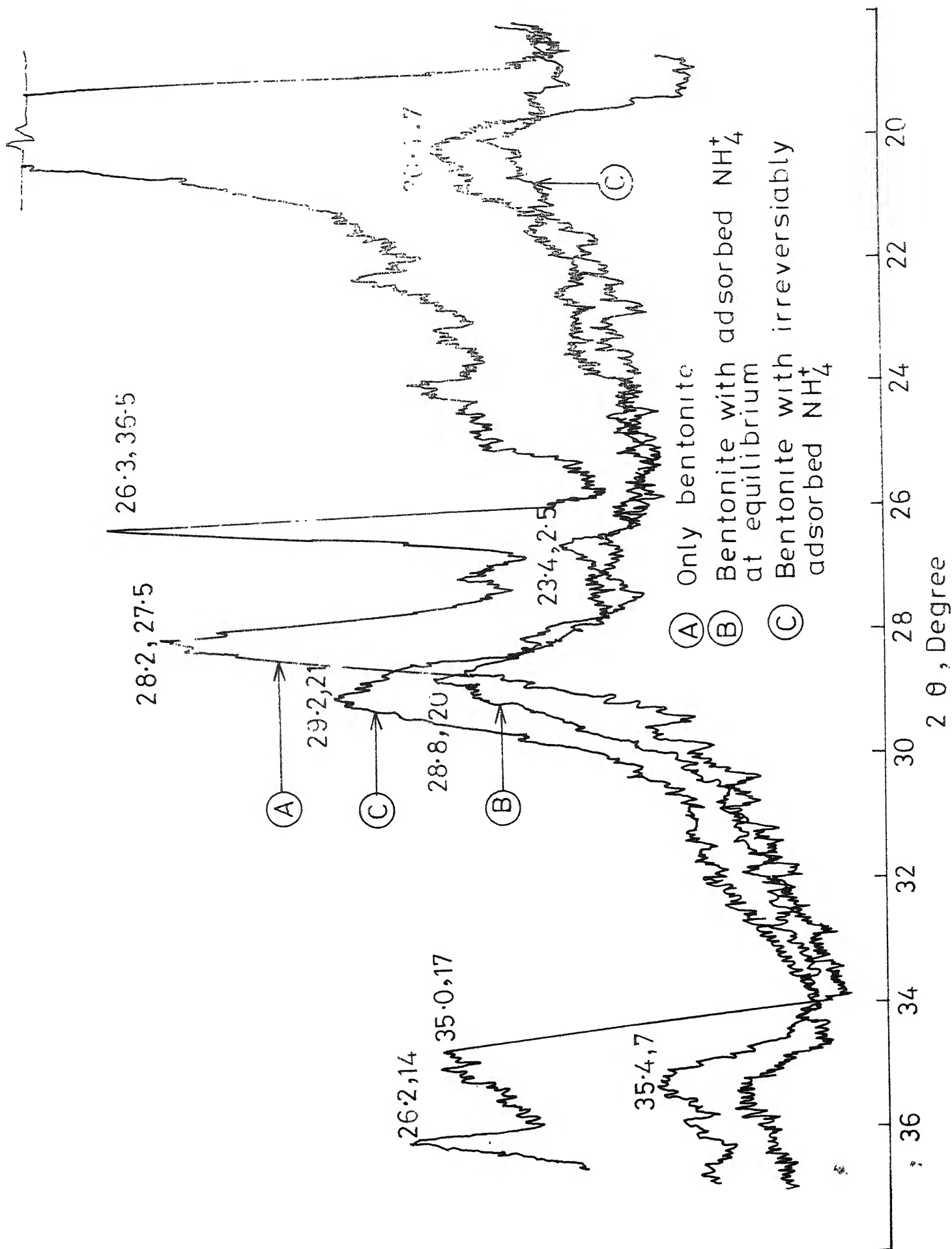


Fig.5.1 X-Ray diffraction pattern for bentonite

(b) NH_4^+ -kaolinite and NH_4^+ -bauxite samples: As can be seen from the Figures 5.2 & 5.3, the characteristic kaolinite peaks at 7.19 \AA and 3.57 \AA have shifted to 7.37 \AA and 3.37 \AA respectively with associated reduction in the intensity of the peaks. In case of bauxite, the shift in the characteristic bauxite peaks is marginal and it can be safely concluded that NH_4^+ ion has not definitely entered the lattice.

5.2.2.2 PO_4^{3-} -clay systems: As can be seen from Figure 5.3, the characteristic kaolinite peaks have shifted from 7.19 \AA and 3.57 \AA to 7.86 \AA and 3.72 \AA with associated decrease in intensities. This increase in basal spacing value conclusively proves presence of PO_4^{3-} ions in the crystal lattice with a coating of PO_4^{3-} ions selectively along the surface.

5.1.3 Cation Exchange Capacity:

Tentative quantitative analysis of the clay mineral composition suggests considerable quantity of inert minerals such as quartz. This explains slight disagreement between the actual C.E.C. values and the values reported in the literature [Olphen (1963)].

5.2 Phase II Studies:

Adsorption studies were conducted in agitated nonflow systems for studying the kinetics, nature and relative extent of adsorption and desorption for all the three minerals at

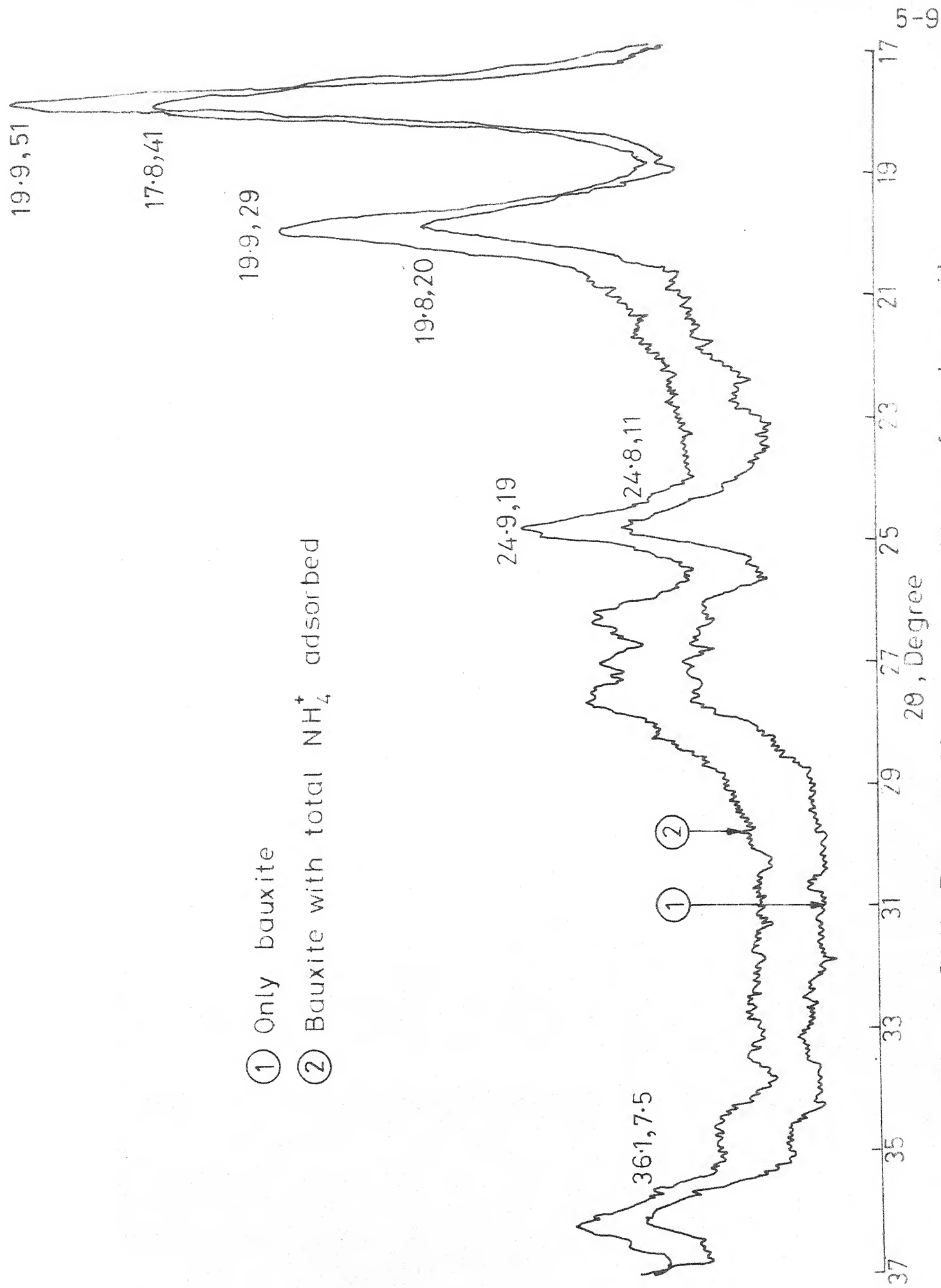


Fig. 5.2 X-Ray diffraction pattern for bauxite

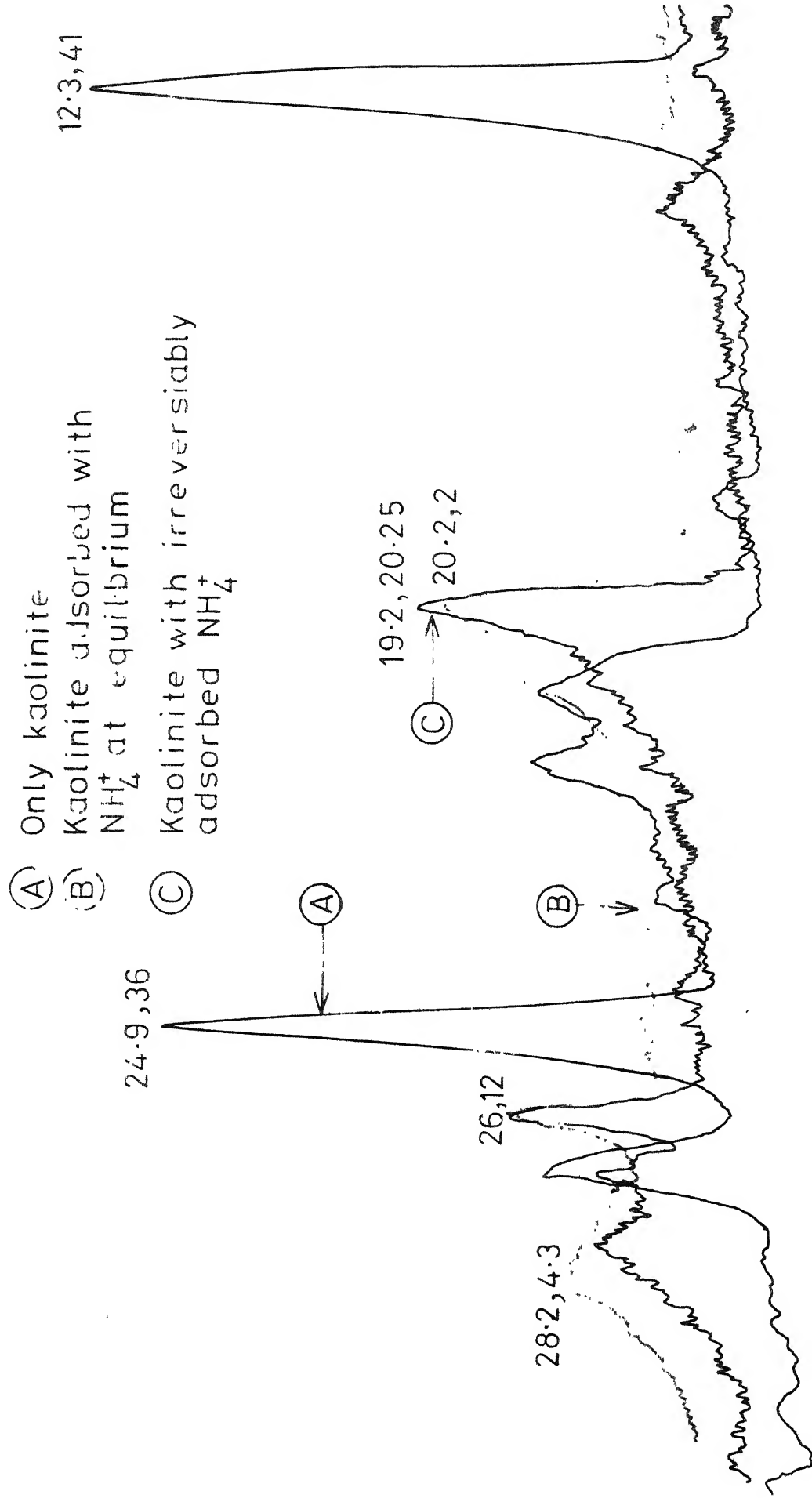


Fig. 5-3A X-Ray diffraction pattern for NH_4^+ -kaolinite system

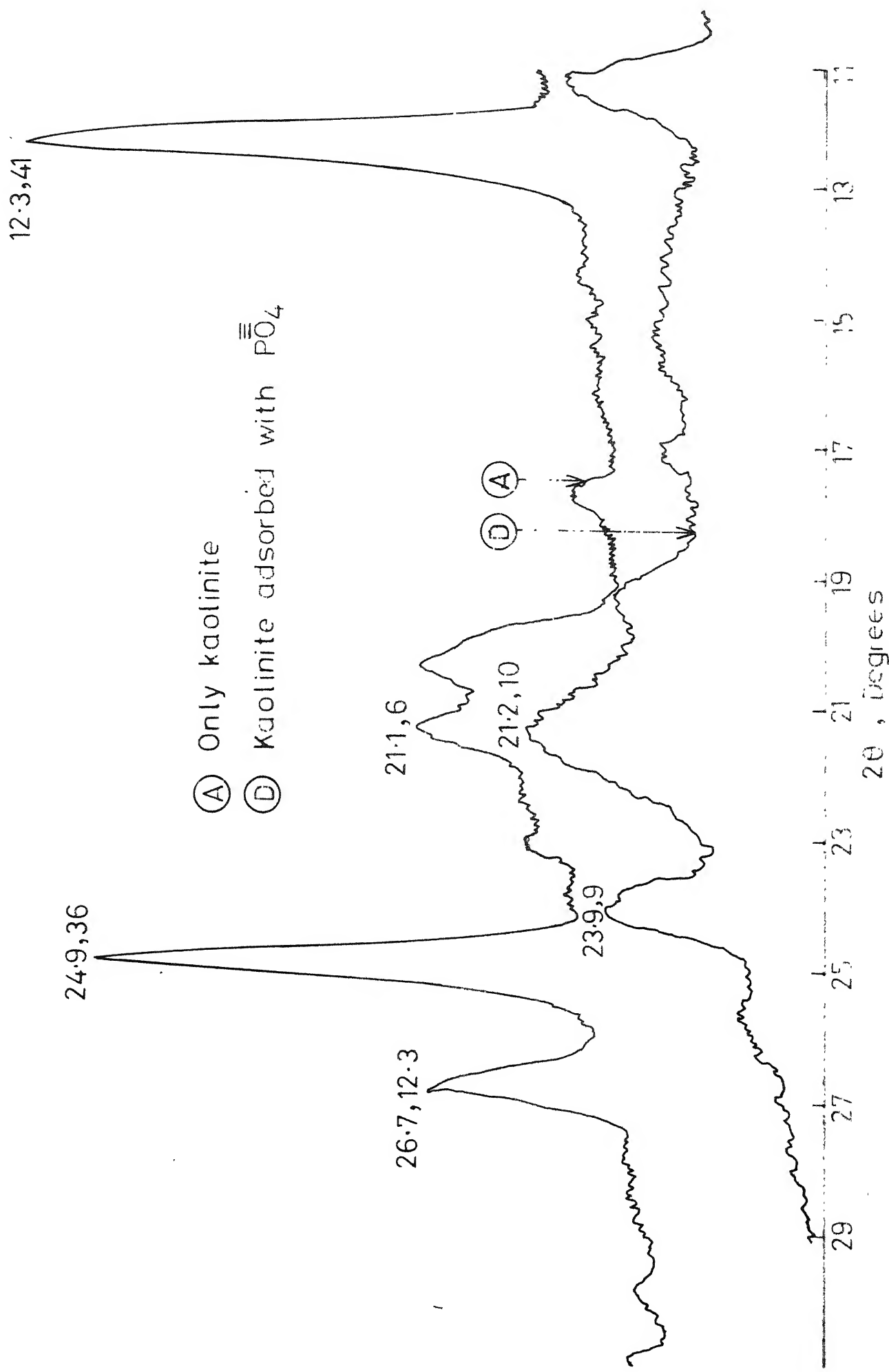


Fig. 5.3B X-Ray diffraction pattern for PO_4 -kaolinite system

three different pH values, the sorbates being NH_4Cl and S.T.P.P. The procedure has been described in Section 4.3.1.2. Rotary shaker run @ 52 r.p.m. was used to provide agitation in all the studies. The shaker could have been run at a higher speed of approximately 100 r.p.m. only for a brief period of time but it is not designed to run at this high speed at a stretch for 12 to 15 hours time which was the average equilibrium time in most of the kinetic studies. Moreover the chosen speed of 52 r.p.m. was visually seen to generate sufficient turbulence to ensure that in the agitated nonflow system, the interparticle diffusion would not limit the adsorption process.

5.2.1 Adsorption Kinetics:

Contact time studies were conducted to illustrate the time dependence of the adsorption process. In a long term adsorption kinetics study it was observed that actually equilibrium is achieved in as long a contact period as 180 hours (Figure 5.4). Similar results have been reported by Morris and Weber (1962) in activated carbon-ABS systems. However, as can be seen from the Figure ^{5.4} for contact times of 2, 12 and 20 hours, the quantity of NH_4^+ ion adsorbed is as high as 87.87%, 92.05% and 94.14% of the ultimate values respectively. Equilibrium is rarely achieved in the most of the practical field conditions [Bernardin (1961)]. In most of the kinetic studies, it was observed that the systems, for

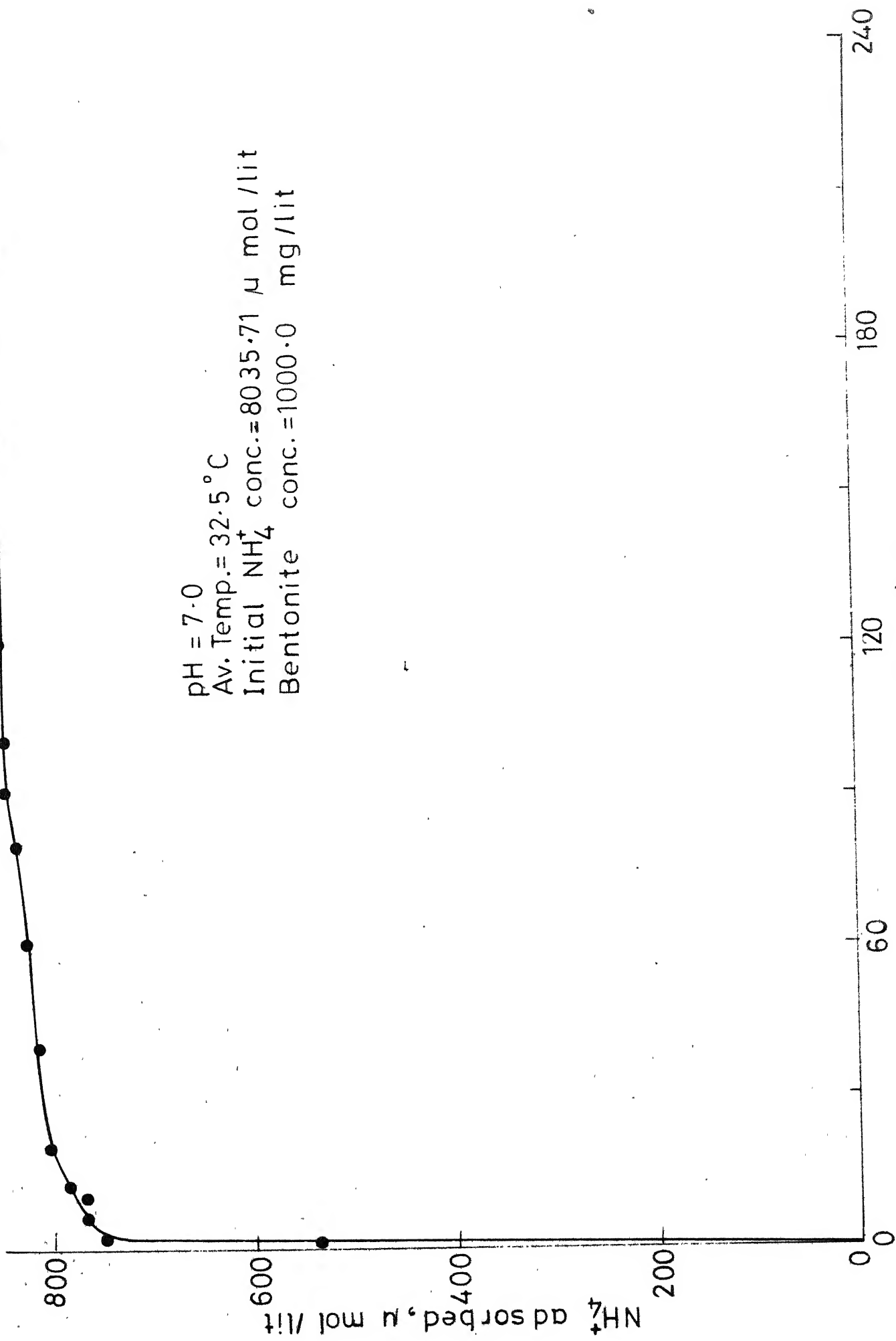


Fig. 5.4 Long term adsorption kinetics with NH_4^+ - bentonite system

all practical purposes, equilibrated between 12 to 20 hours, though extension of these kinetic runs would have yielded comparatively insignificant (quantitatively) adsorption after that time. It was therefore decided that long term kinetic studies need not be conducted and approximating the short term kinetic study equilibrium values to the ultimate values is reasonably accurate and justified.

5.2.1.1 Factors affecting the adsorption kinetics: Various factors affecting adsorption and their significance has been outlined in Chapter 2. However, few of them have been elaborated below as these are relevant.

5.2.1.1.1 Hydrogen ion concentration: The hydrogen ion concentration governs the degree of ionization and the nature of species of various anions and cations present in the system. Thus pH value governs both the kinetics and the ultimate adsorptive capacities in adsorption process. Adsorption kinetics and adsorption isotherms at three different pH values ~~have~~ been studied. Figure 5.5 & 5.6 illustrate the effect of pH on adsorption kinetics.

Scrutiny of Figures 5.5 & 5.6 and also rest of kinetic study plots in Figures 5.8-5.13, reveals that the adsorption of NH_4^+ as well as PO_4^{3-} ions on all the clay minerals proceeds in two distinct phases. In the first phase, the rate of adsorption is very rapid in about first two hours. This is followed by gradual adsorption till equilibrium is reached.

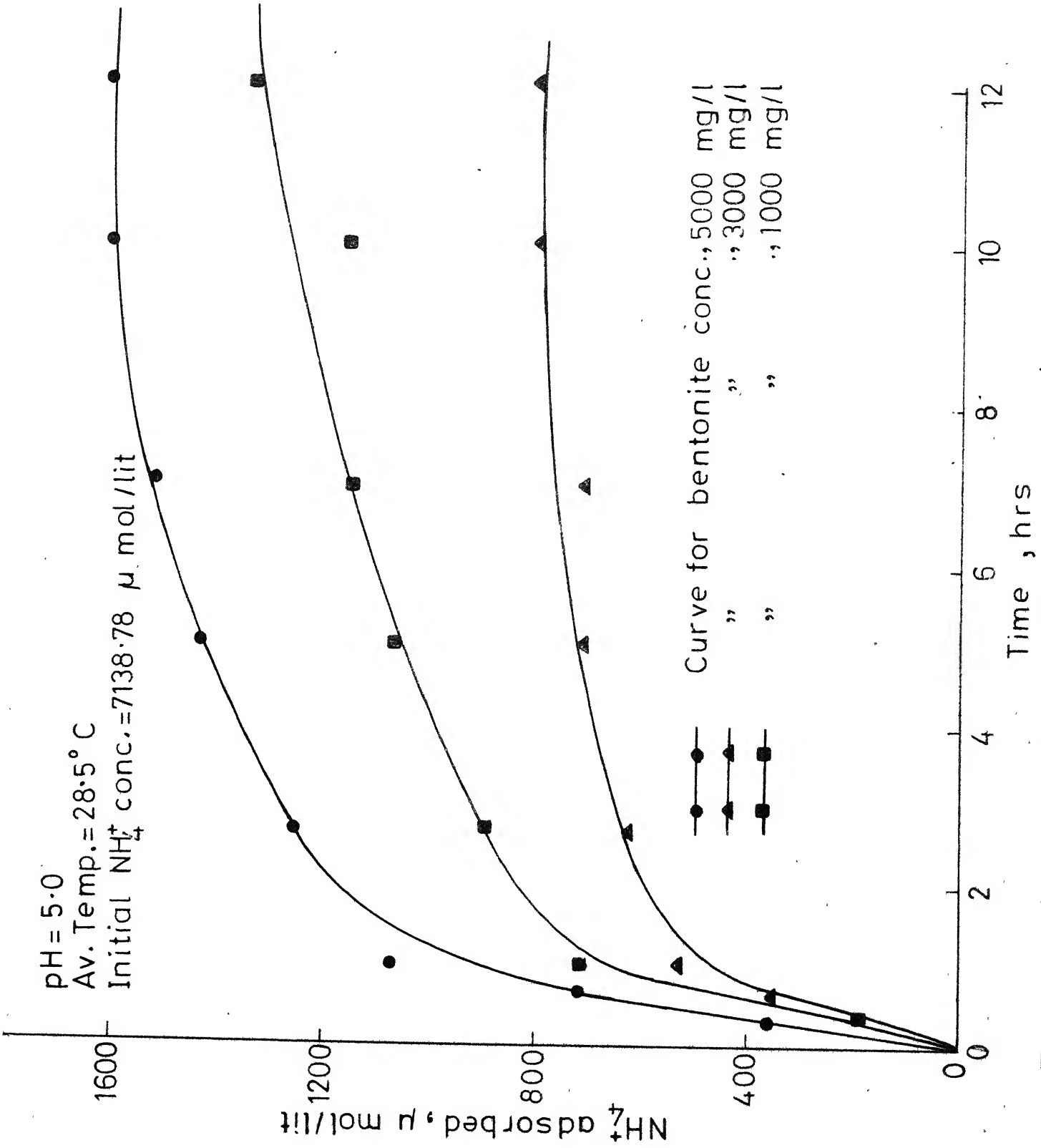
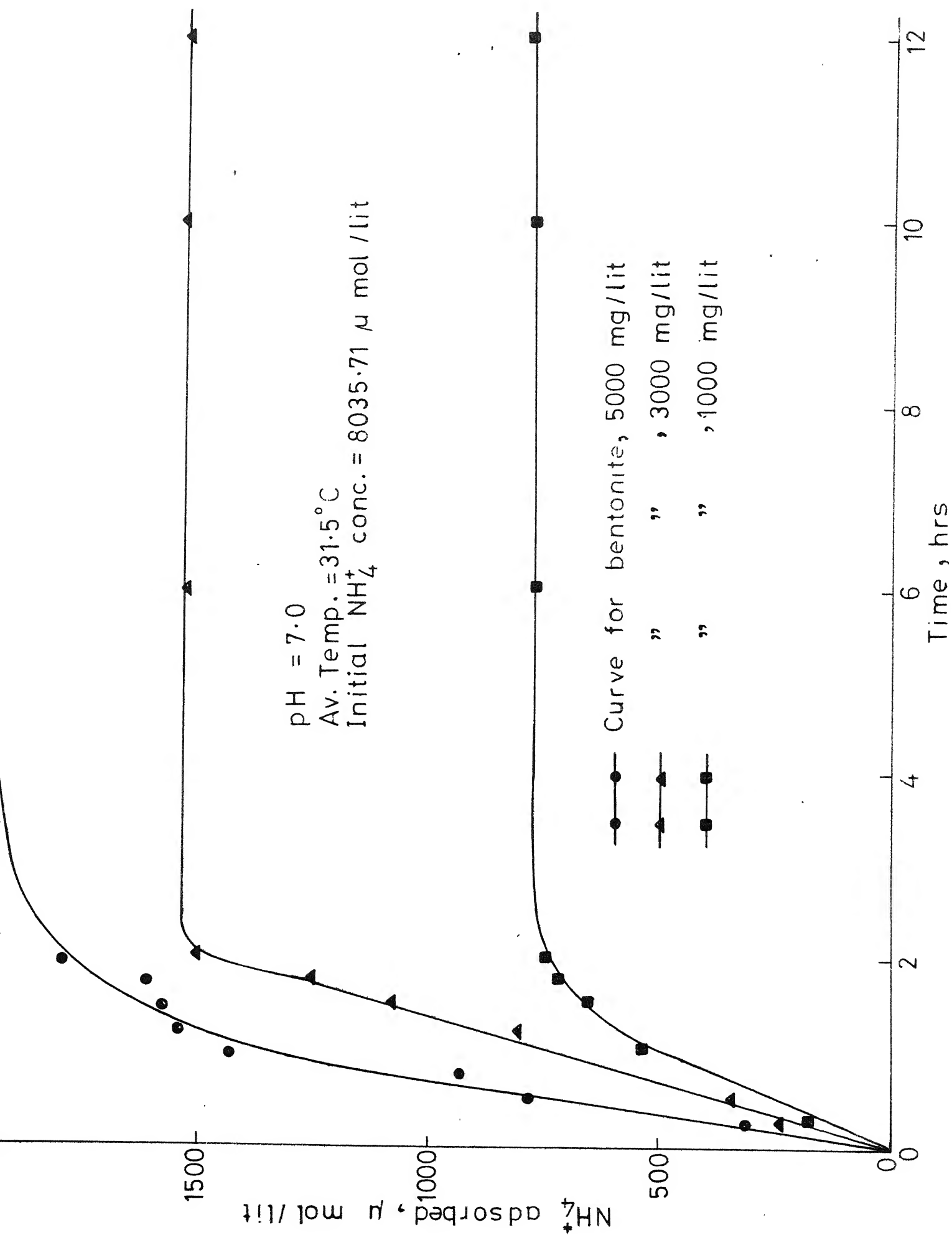


Fig. 5.5 Adsorption kinetics with NH_4^+ -bentonite system

Fig. 5.6 Adsorption kinetics with NH_4^+ - bentonite system

pH = 7.0
 Av. Temp. = 32.0 °C
 Bentonite conc. = 1000.0 mg/lit

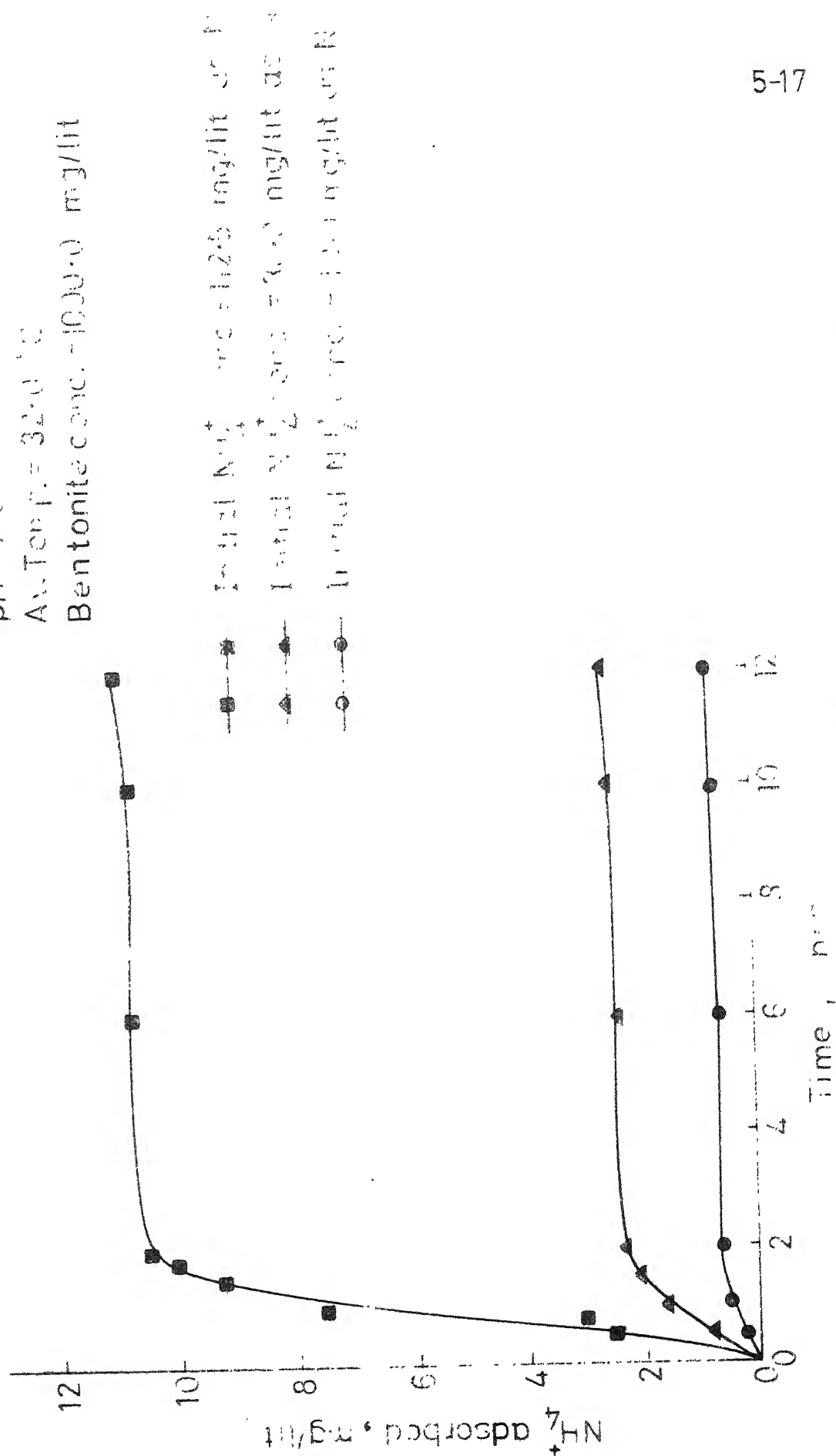


Fig. 5.7 Effect of initial conc. of NH_4^+ on rate and extent of adsorption

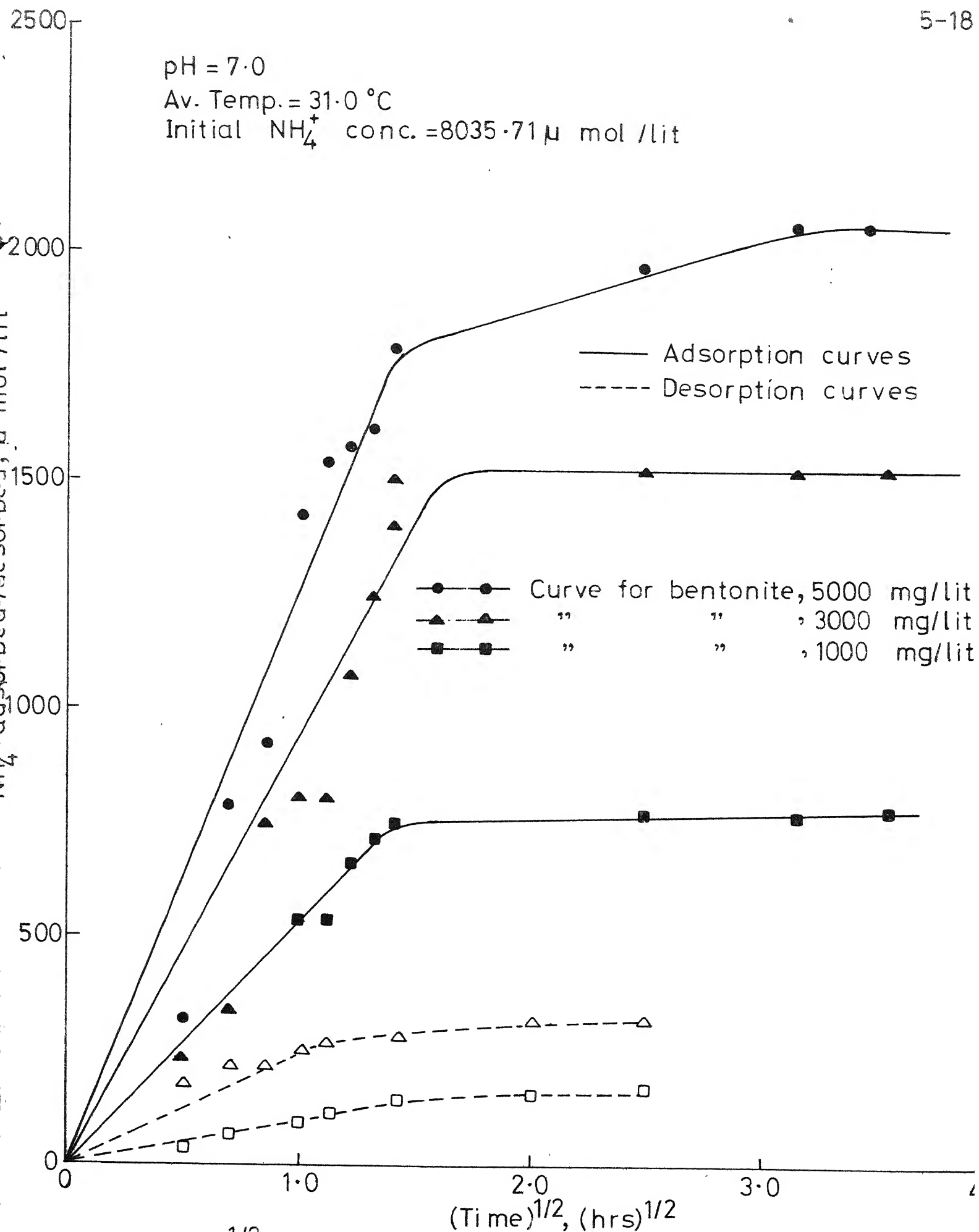


Fig. 5.8 $(\text{Time})^{1/2}$ vs uptake/release plot with NH_4^+ - bentonite system

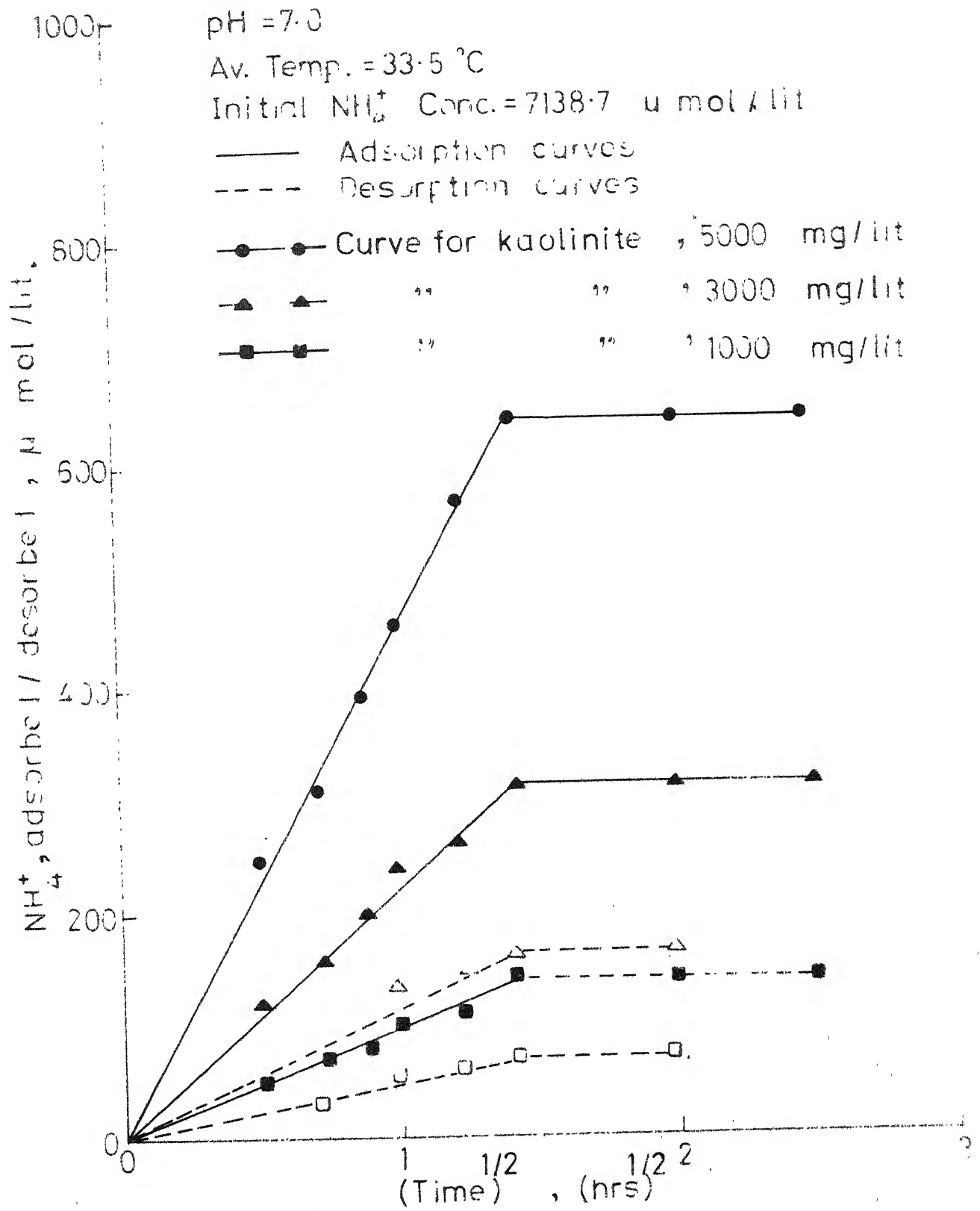


Fig. 5.9 $(\text{Time})^{1/2}$ vs uptake/release plot for NH_4^+ -kaolinite system

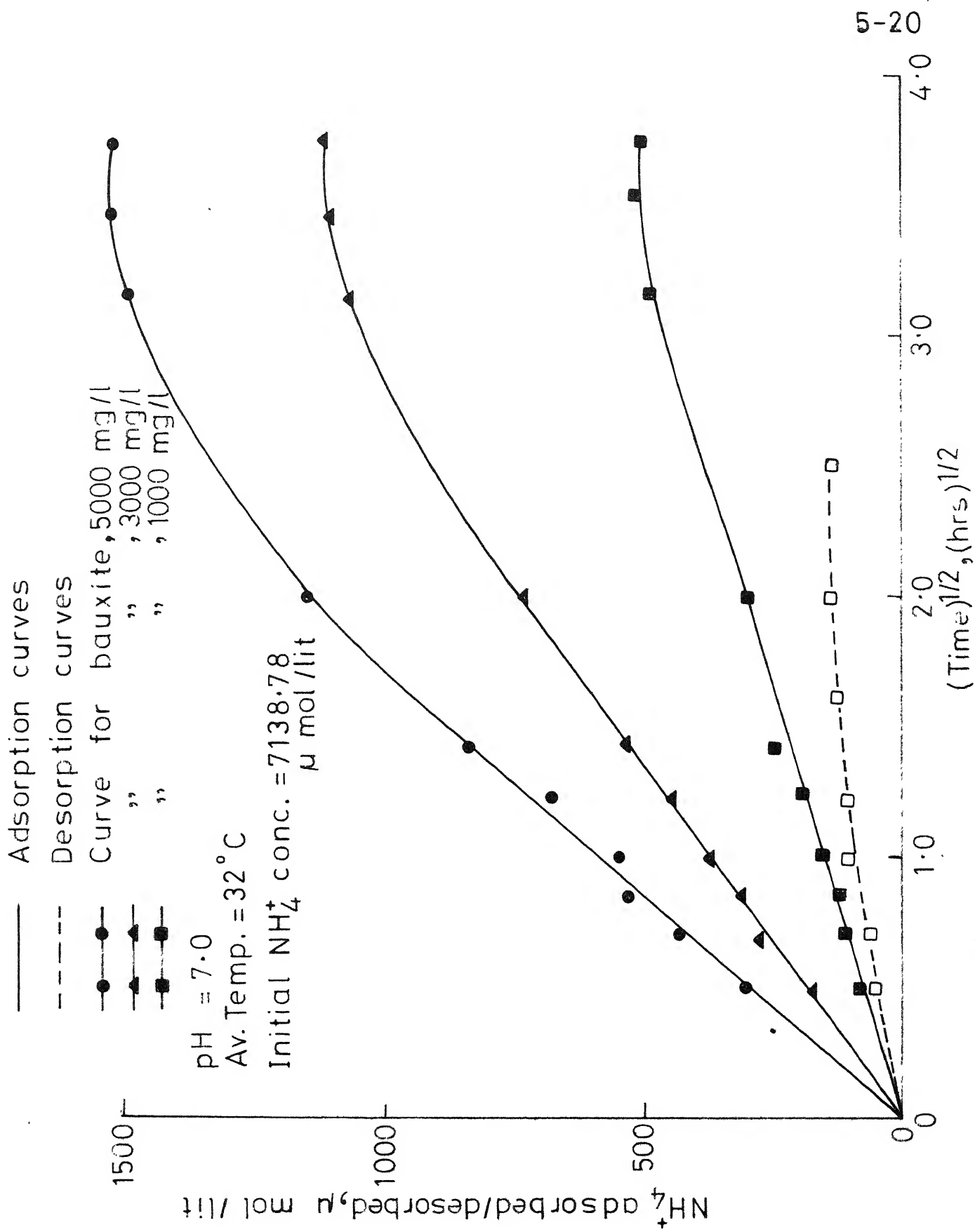


Fig. 5-10 (Time)^{1/2} vs uptake/release plot for NH_4^+ -bauxite system

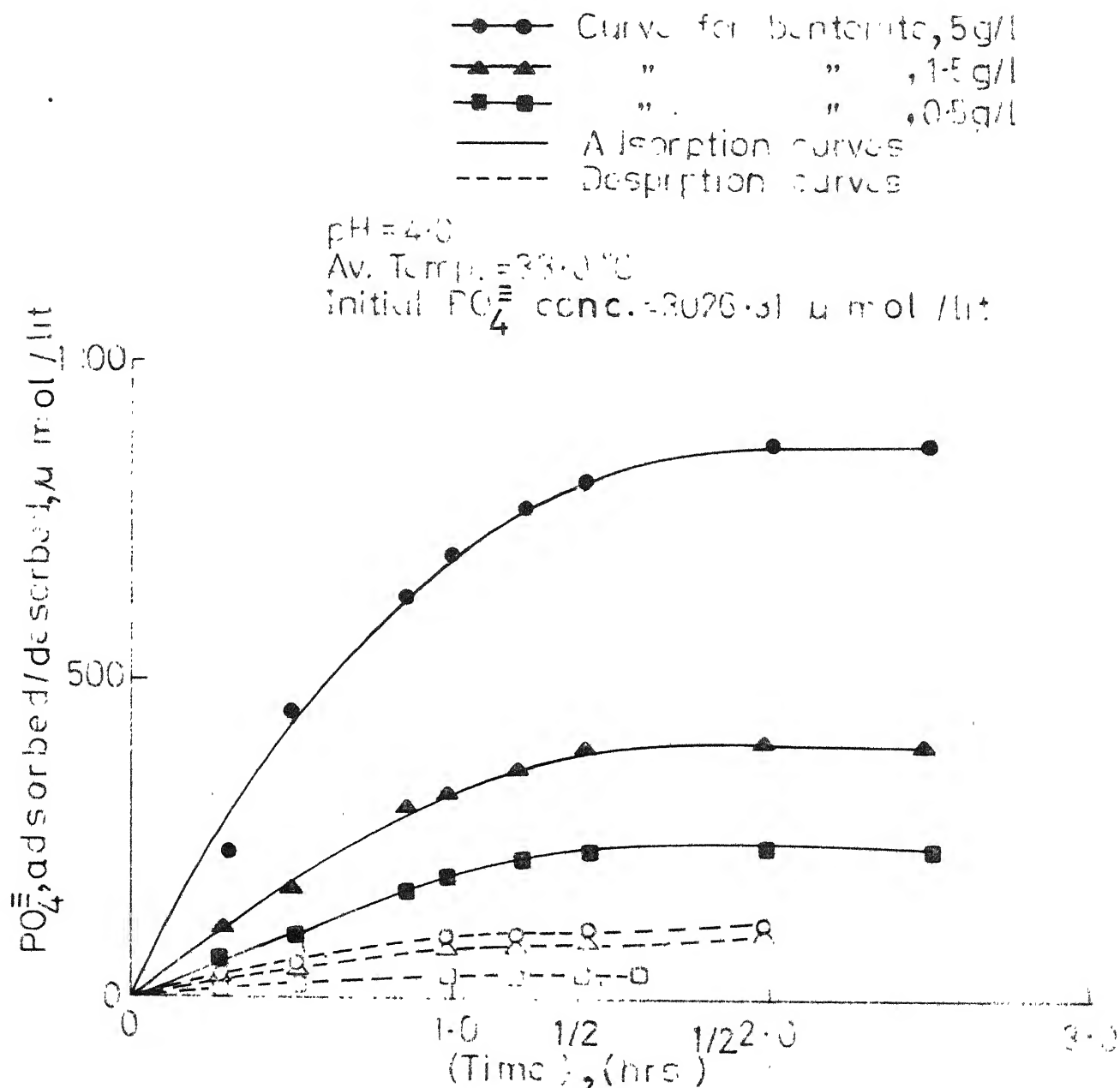


Fig. 5.11 $(\text{Time})^{1/2}$ vs uptake/release plot for PO_4^{3-} - bentonite system

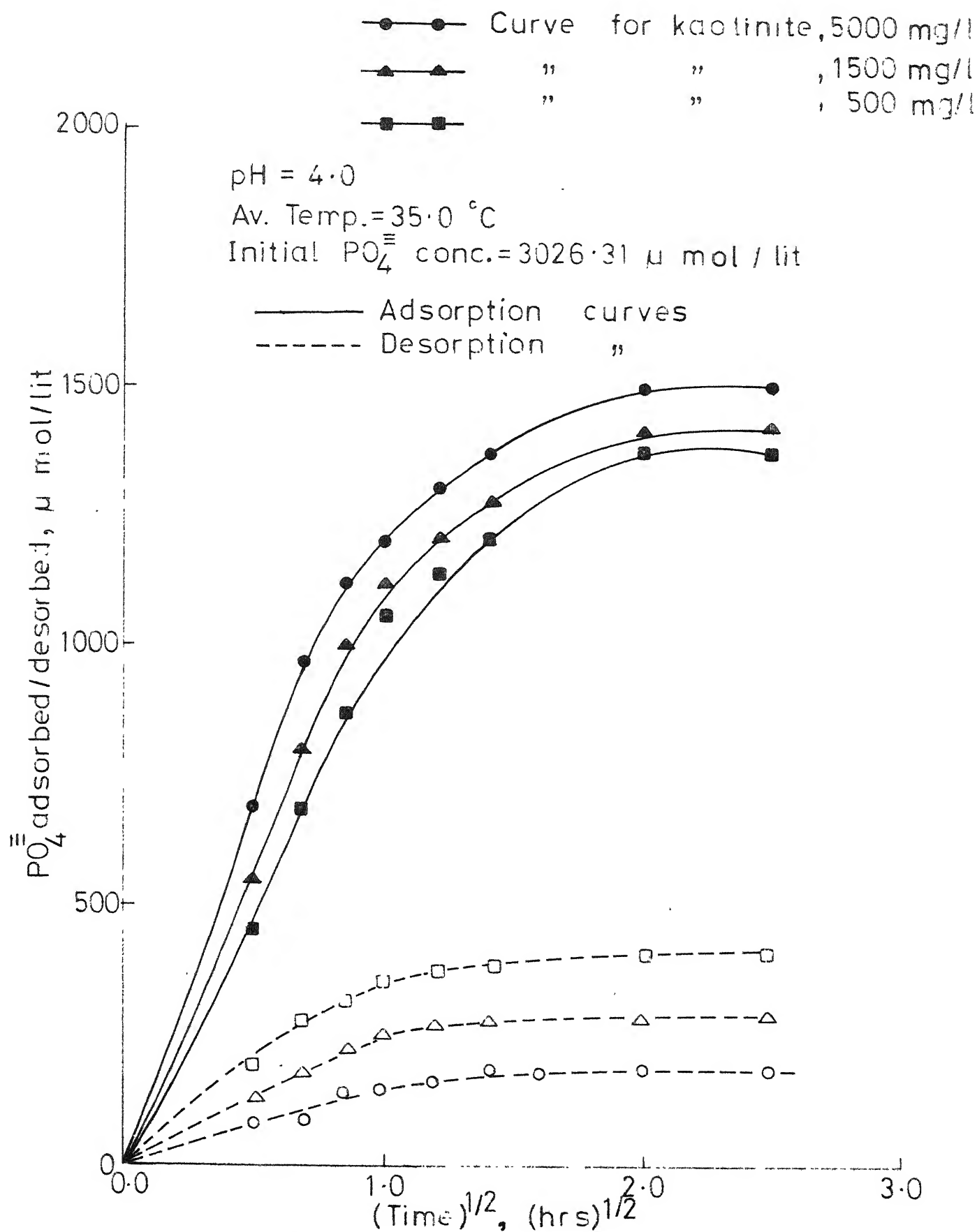


Fig.5.12 (Time)^{1/2} vs uptake/release plot for PO_4^{\equiv} -kaolinite system

pH = 4.0

Av. Temp. = 34.0 °C

Initial $\text{PO}_4^{=}$ Conc. = 3026.31 $\mu\text{mol/lit.}$

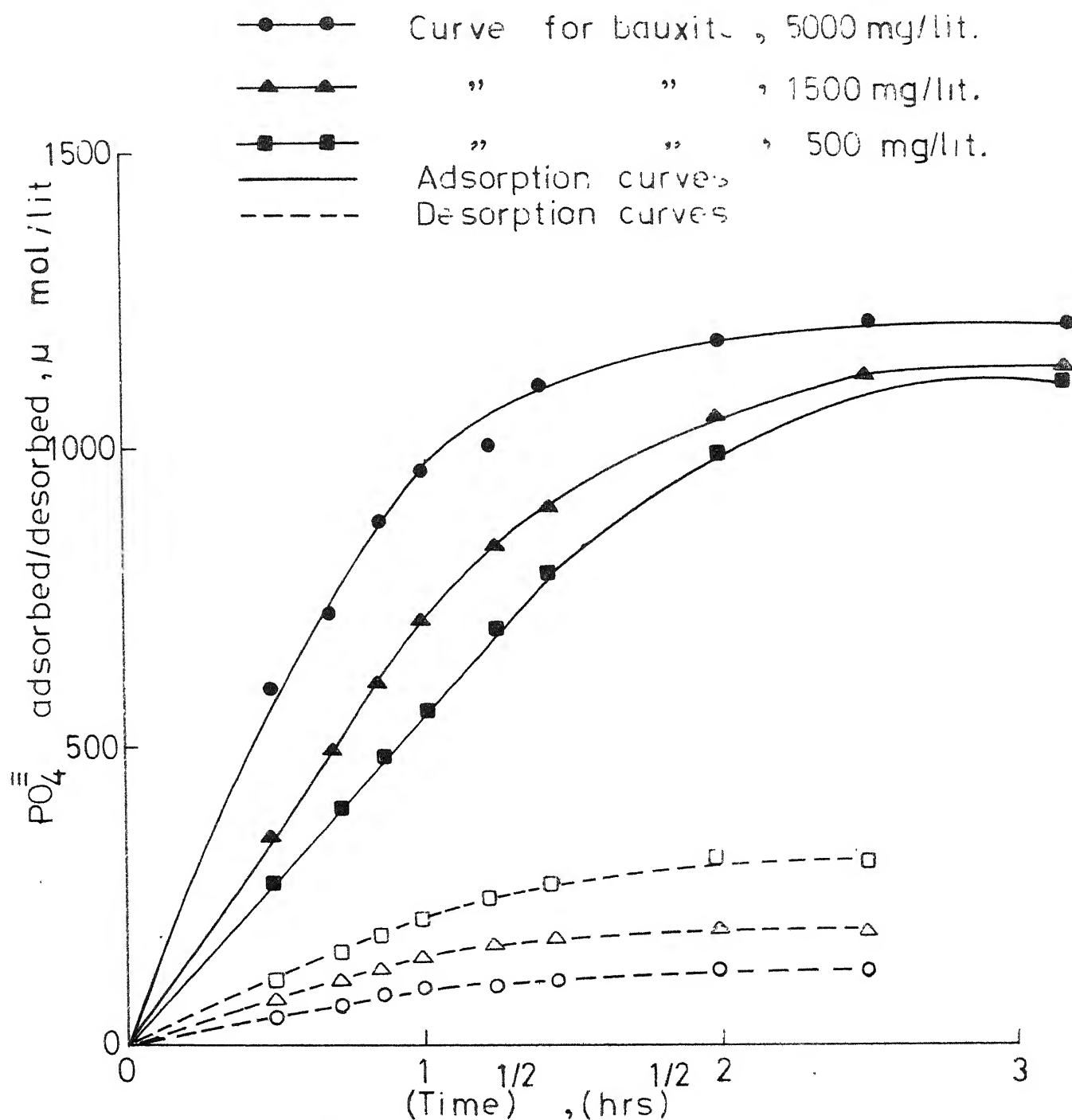


Fig.5.13 Time^{1/2} vs uptake/release plot for $\text{PO}_4^{=}$ -bauxite system

This observation slightly differs from the one reported by Sethu Raman (1973) in that the instantaneous adsorption phase as reported by him, in case of clay minerals-dye systems, is missing in the present study. The other two phases are identical to the ones he has mentioned. Secondly the first phase of adsorption for first one hour or so is so rapid in most of the cases that this phase may be termed as instantaneous adsorption. Table III illustrates effect of pH on the rate of adsorption as well as the adsorptive capacities.

A perusal of Table III reveals that both the rates of adsorption as well as the ultimate adsorptive capacities for NH_4^+ are higher at ^{high} low pH. This is obvious as at lower pH values increased concentration of H^+ ions compete with NH_4^+ ions thereby reducing the rate and extent of adsorption compared to corresponding values at higher pH. ^{At low pH} Ionization & displacement of lattice of OH^- ions ^{to the surface} & competition of H^+ ions with NH_4^+ ions may be taken note of here.

5.2.1.1.2 Surface area: Adsorption is principally a surface reaction and as such the extent of adsorption is proportional to the specific surface area. Specific surface area is that portion of the total area of the adsorbent which is available for adsorption. The total and the specific surface areas in each case have been calculated and tabulated in Table VII.

Surface area available for adsorption is directly proportional to the quantity of adsorbent added. It is evident from Table III that both the adsorption rates and the adsorptive capacities are highest in the case of samples

Table III

Effect of pH on Adsorption Process

NH₄⁺-Bentonite System

Temperature = (30 ± 1.5)°C

pH	Initial NH_4^+ concentration		Rate of adsorption in first 1 hour						NH_4^+ adsorbed at equilibrium					
	mg/l as N	$\frac{\mu\text{moles}}{\text{l}}$	$\mu\text{moles/g-hr}$			$\frac{\text{mg}}{\text{mg min}}^{-1}$			$\mu\text{moles/g}$			mg/mg		
			S ₁	S ₂	S ₃	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃
5.0	128.75	9196.43	214.00	240.00	500.00	6.4x 10 ⁻⁵	7.2x 10 ⁻⁵	1.5x 10 ⁻⁴	321.24	446.17	713.87	5.78x 10 ⁻³	8.03x 10 ⁻³	12.8x 10 ⁻³
7.0	112.50	8035.71	266.00	266.67	535.00	7.98x 10 ⁻⁵	8.0x 10 ⁻⁵	1.6x 10 ⁻⁴	410.71	505.95	785.71	7.39x 10 ⁻³	9.11x 10 ⁻³	14.14x 10 ⁻³

Note: S₁ - Sample with bentonite concentration, 5000 mg/l
 S₂ - Sample with bentonite concentration, 3000 mg/l
 S₃ - Sample with bentonite concentration, 1000 mg/l

wherein the bentonite concentration was the least. This can be explained on the basis of the fact that with higher bentonite concentrations, part of the specific area provided remains unutilized and in case of lower bentonite concentrations, almost the entire specific area is utilized for adsorption. The same trend is observed in rest of the kinetic studies.

5.2.1.1.3 Concentration gradient: Effect of initial concentration of adsorbate on the adsorption process is illustrated in Figure 5.7. The data suggests that the rates of adsorption increase with increasing initial concentrations of adsorbate. ~~Since the concentration gradient is the~~ principle driving force for adsorption. Thus the adsorptive capacities of the minerals could be utilized to their utmost when the solute concentrations are high.

5.2.1.1.4 Temperature: Adsorption reactions are normally exothermic. The rate and extent of adsorption generally increases with decreasing temperatures [Weber (1974)]. However, since small temperature variations generally have a minor effect on the process of adsorption [Weber (1974)], the temperature dependence of adsorption processes in the narrow range of temperatures encountered during the usual environmental adsorption studies are almost negligible.

5.2.2 Rates of Adsorption:

In most of the adsorption reactions, the rate of adsorption is controlled by the rate of diffusion of the solute in the capillary pores of the adsorbent particles. Theoretical treatments of intraparticle diffusion yields rather complex mathematical relationships, which differ in form as a function of the geometry of the adsorbent particle [Morris and Weber (1962)]. An empirically found functional relationship common to most adsorption processes is that the uptake varies almost proportionately with the time raised to power $1/2$ ($t^{1/2}$), rather than with t [Weber, 1971]. Figures 5.8 -5.13 amply demonstrate this fact. These figures indicate the uptake of NH_4^+ and PO_4^{3-} ions as a function of $t^{1/2}$ for all the NH_4^+ -clay and PO_4^{3-} -clay systems at selected pH values. Figures 5.8 & 5.9 indicating the kinetics for NH_4^+ -bentonite and NH_4^+ -kaolinite system show a striking similarity. Good linearization in both the segments is obtained from the data. Thus intraparticle diffusion largely controls the adsorption rate in both the phases as described in Section 5.2.1.1. In the second phase also, owing to the linearized form of the kinetics curve, pore diffusion only is the likely rate limiting step. Comparatively lower rate of adsorption is observed because when the easily available sites are occupied the subsequent adsorption process encounters more resistance which slows its process rate. Figure 5.10 indicating the NH_4^+

uptake as a function of $t^{1/2}$ and Figures 5.11-5.13 respectively indicating similar parameters in PO_4^{3-} -bentonite, PO_4^{3-} -kaolinite and PO_4^{3-} -bauxite systems also show a striking similarity. In the first rapid phase of adsorption, good linearization of the data is observed. The slow adsorption phase yields a curve instead of a straight line. Thus in these cases, intraparticle diffusion largely controls the rate of adsorption in the first rapid phase and the interparticle diffusion largely controls the rate in the slow adsorption phase because of curvilinear nature of the plot in this phase. Table IV gives a comparative statement of the rates in these phases and also the adsorptive capacities in all the NH_4^+ -clay and PO_4^{3-} -clay systems studied.

5.2.3 Evaluation of the Rate Limiting Step:

In any adsorption process, the knowledge of the rate limiting step in the system is required for designing the necessary facilities for maximum efficiency with minimum possible contact time. There are three consecutive steps in the adsorption of materials from solution by sorbents [Weber, (1974)]. The first of these is the transport of the adsorbate through a surface film to the exterior of the adsorbent or the 'film diffusion'. The second phase involves the diffusion of the adsorbate within the pores of the adsorbent or the 'pore diffusion'. Third and final step is adsorption of the

solute on the interior surfaces binding the pores and the capillary spaces of the adsorbent.

As shown by Weber and Morris (1962), the kinetic experimental data may be used to determine the rate limiting step. In most of the nonflow agitated systems, as the particles are subjected to vigorous agitation, it is probably reasonable to presume that the adsorption rate is not controlled by mass transfer from the liquid bulk to the particle external surface. It is therefore logical to presume that the rate of adsorption is controlled by the intraparticle diffusion or the diffusion of sorbate in the intraparticle pore spaces. A functional relationship common to most adsorption processes is that uptake varies almost proportionately with $t^{0.5}$ rather than with t . Such a variation can be found in both the phases in Figures 5.8-5.9 indicating that intraparticle diffusion (pore) diffusion is the dominating factor signifying the rate limiting step in both the phases of adsorption. Figures 5.10-5.13 show a good linearization in the first rapid phase of adsorption indicating pore diffusion as the rate controlling step in this phase. Good linearization in the second phase of slow adsorption in all these cases is not observed. This indicates that in the second phase interparticle diffusion (film diffusion) is the dominant factor signifying the rate limiting step.

5.2.3.1 Interruption test for evaluation of the rate limiting step: Interruption test is one of the experimental techniques used for distinguishing between the film diffusion and the pore diffusion [Michelson et al. (1964)]. In a regular kinetic study the kinetic run was briefly interrupted once in each of the two observed adsorption phases, by separating the adsorbent clay particles from the solution by centrifugation. After a total interruption period of 1 hour each, the sorbent was reimmersed in the system and the kinetic run was continued. The uptake values just before and after the interruption were observed at close intervals. Figure ^{5.14} shows the results of the interruption test for NH_4^+ -bentonite system. Any increase in the rate of adsorption immediately after the interruption indicates 'pore diffusion' because during interruption period also the diffusion from the surface film to the intraparticle pores continues and immediately on reimmersion, the rate is higher than that before interruption. Practically no change in the adsorption rate before and after the interruption indicates film diffusion as the process does not continue during interruption period because of absence of any concentration gradient. Basic data for Figure ^{5.14} has been included in the Appendix. Referring to Figure ^{5.14} and the data in the Appendix, it is observed that the rate of adsorption just 15 min before ^{interruption} adsorption is

$$\frac{0.60 - 0.50}{0.25} = \frac{0.10}{0.25} = 0.4 \text{ hour}^{-1}$$

pH = 7.0
 Av. Temp. = 32.5 °C
 Bentonite conc. = 5000 mg/lit

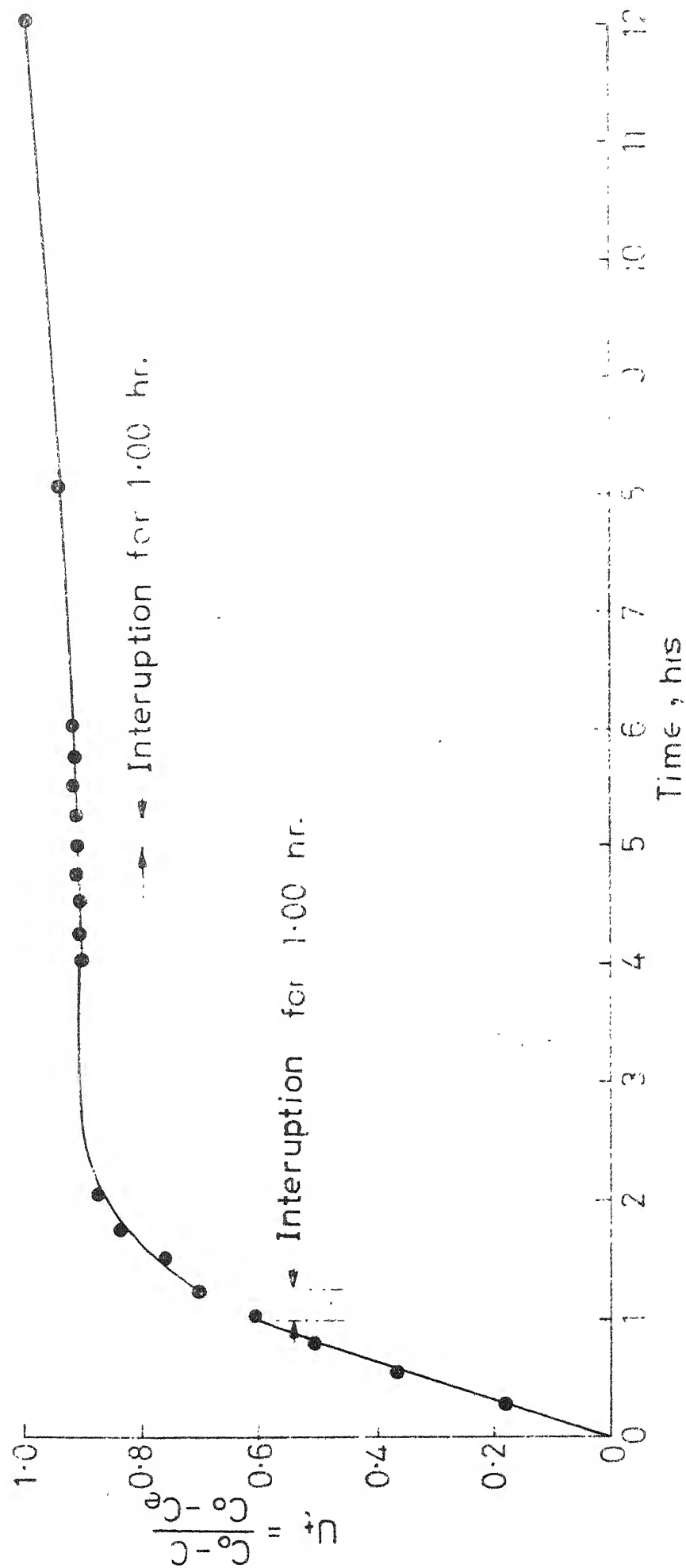


Fig 5.14 Interruption test for NH_4^+ bentonite system

And the rate immediately after interruption is

$$\frac{0.7083 - 0.6000}{0.25} = \frac{0.1083}{0.25} = 0.43 \text{ hour}^{-1}$$

This slight increase in the uptake rate is not very significant but indicates pore diffusion as the rate controlling step.

The uptake rates in the second adsorption phase are so small in magnitude that the obvious conclusion from practically unchanged uptake rate after interruption in this phase, 'that film diffusion is the rate limiting step', may be deceptive. Presence of small concentration gradients accounts for the fact that there exists a complex combination of operative mechanisms rather than the reaction being governed by a single operative mechanism. Owing to the small concentration gradients involved, as the above interruption test failed to give substantial information about the rate limiting step, the earlier test giving uptake rate Vs. $t^{0.5}$ was considered sufficiently indicative and the interruption test was not repeated for other sorbate-clay systems.

Bentonite being a three layered mineral, pore diffusion can^{bc} be expected to be the dominant rate controlling mechanism as has been confirmed by the results. Combining the observations of the uptake rate Vs. $t^{0.5}$ plots in Figures 5.8-5.13, the result of the interruption test in Figure 5.14 and the observation of the X-ray powder data as discussed in Section 5.1.2, it is concluded that 'intraparticle diffusion'

(pore diffusion) is the dominant factor deciding the rate controlling step in all the phases of adsorption in Figures 5.8 - 5.13, except the second slow phases of adsorption in Figures 5.10-5.13 wherein interparticle diffusion (film diffusion) is the operative rate limiting step. Table IV gives a comparative statement of the uptake rates in various phases of adsorption for the NH_4^+ -clay and PO_4^{3-} -clay systems. It can be seen from the table that barring phase II for NH_4^+ -bentonite system, the general trend in all the phases is increasing adsorption rate as expressed in $\text{mg/g (hr)}^{1/2}$ with decreasing clay concentrations.

This observation is consistent with the results in Table III and the same argument of better solute-sorbent contact holds here. Although the 'K' values thus obtained do not have usual dimensions for rate constants and cannot be so termed, relative values for approximately similar conditions are significant as rate parameters [Morris and Weber (1962)].

5.2.4 Desorption Studies:

At the end of kinetic studies, fully saturated clay particles were separated from the system by centrifugation, oven-dried @ 105°C ., for 24 hours and redispersed in distilled water of volumes calculated on the basis of the necessary corrections for loss of the clay particles during all the above operations thereby maintaining the same sorbent concentration as during the corresponding kinetic studies.

Table IV

Comparative Statement of Adsorption Rates During Kinetic Studies

Temperature = $(33 \pm 2)^{\circ}\text{C}$

Solute-sorbent system	Average adsorption rates 'K'												Speculated rate limiting step	
	Phase I						Phase II							
	$\mu\text{moles/g}(\text{hr})^{1/2}$						$\mu\text{moles/g}(\text{hr})^{1/2}$							
	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3	Phase I	Phase II
NH_4^+ -bentonite	254.28	312.50	535.71	4.58	5.62	9.64	26.92	3.40	9.26	0.48	0.06	0.76	Pore diffusion	Pore diffusion
NH_4^+ -kaolinite	52.46	84.70	114.75	0.94	1.52	2.06	-	-	-	-	-	-	"	"
NH_4^+ -bauxite	116.90	125.58	150.00	2.10	2.26	2.70	43.68	72.80	114.94	0.78	1.31	2.07	"	Film diffusion
PO_4^{3-} -bentonite	175.00	233.34	400.00	3.15	4.20	7.20	49.52	140.74	121.04	0.89	2.53	2.18	"	"
PO_4^{3-} -kaolinite	270.00	761.90	1942.84	4.86	13.71	34.97	49.41	224.62	761.10	0.88	4.13	13.70	"	"
PO_4^{3-} -bauxite	300.00	480.00	1120.00	5.40	8.64	20.16	40.62	158.11	509.26	0.73	2.89	9.17	"	"
Note:	S1	-	Sample with clay concentration, 5000 mg/l							(10,000 mg/l only for kaolinite sample)				
	S2	-	Sample with clay concentration, 3000 mg/l							For NH_4^+ -clay systems.				
	S3	-	Sample with clay concentration, 1000 mg/l											
	S1	-	Sample with clay concentration, 5000 mg/l											
	S2	-	Sample with clay concentration, 3000 mg/l							For PO_4^{3-} -clay systems.				
	S3	-	Sample with clay concentration, 1000 mg/l											

The desorption kinetic curves are incorporated in Figures 8 to 13 along with the adsorption kinetic curves only.

As in the adsorption kinetic curves, two distinct phases of desorption are observed here also. The desorption rates are much lower than the corresponding adsorption rates and equilibrium is attained much earlier than in case of adsorption kinetics runs. Table V gives a comparative state-
its
ment of desorption rates and extent in all the systems.

Figures 5.15 to 5.17 give a graphical representation of the amounts of NH_4^+ adsorbed, desorbed and irreversibly retained in case of NH_4^+ -bentonite, NH_4^+ -kaolinite and NH_4^+ -bauxite systems respectively. Basic data for these figures has been included in the Appendix.

These figures indicate that the adsorption equivalent to the cation exchange capacity of the clays is irreversible, for the concentrations used. The whole of the remaining quantities of NH_4^+ adsorbed over and above the cation exchange capacity is not fully desorbed but a fraction of it still stays adsorbed. The quantity of NH_4^+ adsorbed may be attributed to physical adsorption which is reversible, whereas the balance may be attributed to physico-chemical adsorption including the monolayer which is not easily desorbed [Weber (1972)].

This point has been further elaborated in this very chapter after the calculations of surface areas and speculated number of layers of NH_4^+ and PO_4^{3-} ions around the particles.

Table V

Comparative Statement of Rates of Desorption

Solute-sorbent system	Average desorption rate												Amount desorbed @ equilibrium							
	Phase I						Phase II						$\mu\text{moles/l}$			mg/l				
	$\mu\text{moles/g}(\text{hr})^{\frac{1}{2}}$						$\text{mg/g}(\text{hr})^{\frac{1}{2}}$													
	$\mu\text{moles/g}(\text{hr})^{\frac{1}{2}}$			$\mu\text{moles/g}(\text{hr})^{\frac{1}{2}}$			$\text{mg/g}(\text{hr})^{\frac{1}{2}}$			$\text{mg/g}(\text{hr})^{\frac{1}{2}}$										
	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃					
NH ₄ ⁺ - <u>bentonite</u>	-	83.34	100	-	1.50	1.80	-	23.34	60	-	0.42	1.08	-	320	160	-	1.92	2.88		
NH ₄ ⁺ - <u>keolinite</u>	-	38.10	50	-	0.88	0.90	-	-	-	-	-	-	-	210	70	-	1.26	1.26		
NH ₄ ⁺ - <u>bauxite</u>	-	-	100	-	-	1.80	-	-	40	-	-	0.72	-	-	140	-	-	2.52		
PO ₄ ³⁻ - <u>bentonite</u>	20	53.34	60	0.36	0.96	1.08	4	13.34	20	0.07	0.24	0.36	120	100	40	0.43	1.19	1.44		
PO ₄ ³⁻ - <u>keolinite</u>	-	-	70	168.67	300	1.26	3.00	5.40	12	15.00	50	0.21	0.27	0.90	410	280	180	1.48	3.36	6.48
PO ₄ ³⁻ - <u>bauxite</u>	44	100.00	200	0.79	1.80	3.60	18	26.67	40	0.32	0.48	0.72	305	190	120	1.10	2.28	4.32		

* S₁, S₂, S₃ etc. as defined in Table IV.

- No desorption observed.

5.2.5 Adsorption Equilibria Studies:

Adsorption equilibria experiments were conducted for obtaining the adsorptive capacities of the adsorbents used at three pH values. This was done to identify the sorbent with optimum adsorptive capacities with regards to both NH_4^+ and PO_4^{3-} ions and the corresponding optimum pH value(s). In case of NH_4^+ -clay systems the pH values selected were, 7.0, 5.0 and 3.0. Adsorption studies in the basic pH range were not done because it is in this range, that the percentage of free NH_3 (gas) in the solution goes on increasing with increasing pH and any ammonia stripping at higher pH values might be mistaken as equivalent NH_4^+ adsorbed by the clays. In the acidic pH range, the percentage of dissociated ammonia (NH_4^+ ion) in an aqueous solution is near hundred percent [Loher (1973)].

At pH = 7 and Temperature = 25°C

NH_4^+ percentage is 97.5%, at pH = 10 and Temperature = 25°C,
it is only 15.4%

whereas at pH = 11 and Temperature = 25°C,
it is just 1.8% [Loher (1973)].

For PO_4^{3-} -clay systems, the pH values chosen were 4, 7 and 10.

At pH = 4, the predominant ion is H_2PO_4^- with insignificant amounts of H_3PO_4 .

At pH = 7, predominant ions are HPO_4^{2-} and H_2PO_4^- whereas at pH = 10, the predominant species is HPO_4^{2-} with traces of PO_4^{3-} [Wayman (1963)]. The ultimate adsorptive capacities are tabulated in Table VI and the basic data has been included in the appendix.

The adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature [Weber (1972)]. Each point on the adsorption isotherm curve therefore represents the equilibrium of an independent sorbate-sorbent system with a particular ratio (by weight) with each other. Adsorption isotherms, thus may be obtained in two ways:

- (1) By keeping the concentration of the solute constant and varying the concentration of the sorbent, and
- (2) By keeping the sorbent concentration constant and varying the solute concentration.

Though selection of one of the above methods is a matter of choice, the former has a distinct advantage of having the same initial solute concentration in all the reagent bottles including the blank in a particular batch test, whereas in the latter, because of varying concentrations of solute in the reagent bottles, the amount of solute adsorbed by the reagent bottles till equilibrium is reached, is likely to vary owing to varying sorbate concentration gradients. It was precisely for this reason that the former was preferred to the latter.

Table VI

Ultimate Adsorptive Capacities of Clay Minerals

Temperature - $(32.5 \pm 2.5)^{\circ}\text{C}$

Clay mineral	NH ₄ ⁺ adsorbed				PO ₄ ³⁻ adsorbed							
	pH = 7.0		pH = 5.0		pH = 3.0		pH = 10.0		pH = 7.0		pH = 4.0	
	$\frac{\mu\text{moles}}{\text{g}}$		$\frac{\mu\text{moles}}{\text{g}}$		$\frac{\mu\text{moles}}{\text{g}}$		$\frac{\mu\text{moles}}{\text{g}}$		$\frac{\mu\text{moles}}{\text{g}}$		$\frac{\mu\text{moles}}{\text{g}}$	
	mg/g		mg/g		mg/g		mg/g		mg/g		mg/g	
Bentonite	1267.96	22.82	714.00	12.85	607.16	10.93	315.76	29.99	368.42	35.00	473.68	45.00
Kaolinite	157.14	2.83	142.86	2.57	71.42	1.28	631.56	60.00	2315.76	220.00	3157.88	300.00
Bauxite	785.72	14.14	571.40	10.28	500.00	9.00	505.24	48.00	1852.64	176.00	2526.32	240.00

However, it was later on found out that because of the comparatively low adsorptive capacities of the clay minerals compared to the adsorbents such as activated carbon, for the chosen solute concentrations, even with as high a sorbent concentration as 7.5 g/l, the equilibrium concentrations did not fall below a particular value and as such the variation of adsorption with concentration at low concentration ranges was not found. With the ultimate adsorptive capacities - the main objects of adsorption studies - already known, the variation of adsorption with low concentration ranges was found out by the second method mentioned above for only one pH value in each case. Combining the results of the two is logically correct, since, after all each and every point on the isotherm represents equilibrium of an independent sorbate-sorbent system with a fixed ratio (by weight) with each other. This was done to compare the observed isotherms with standard isotherm models viz. Langmuir, BET's and the Freundlich. The Langmuir isotherm is of the form,

$$q_e = \frac{Q^0 b C}{1 + bC} \quad (5.1)$$

where

q_e = Number of moles of solute adsorbed per unit weight of sorbent at concentration 'C'.

Q^0 = Number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the adsorbent surface.

C = Measured concentration of solute at equilibrium in moles/l.

b = A constant related to the energy or net enthalpy.

The Langmuir model is based on the assumption that:

- (a) The adsorption at saturation corresponds to a monolayer of solute over the adsorbent surface,
- (b) Energies of adsorption are uniform over the surface, and
- (c) There is no transmigration of sorbate in the plane of the surface.

Linearized form of Langmuir isotherm is as follows:

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \left(\frac{1}{Q^\circ b}\right) \cdot \frac{1}{C} \quad (5.2)$$

The BET's isotherm refers to a multilayer adsorption, the rest of the assumptions in this model being the same as for Langmuir isotherm. It is of the form:

$$q_e = \frac{B C Q^\circ}{(C_S - C) \left[1 + (B - 1) \left(\frac{C}{C_S} \right) \right]} \quad (5.3)$$

where

B = A constant expressive of energy of interaction with the surface.

C_S = Saturation concentration of the solute.

The rest of the symbols have the same significance as for Langmuir model. The linearized form of BET's isotherm is:

$$\frac{C}{(C_S - C)q_e} = \frac{1}{BQ^0} + \left(\frac{B-1}{BQ^0}\right)\left(\frac{C}{C_S}\right) \quad (5.4)$$

The Freundlich model is a special case for heterogeneous surface energy. It relates with the Langmuir model such that the energy term b , in the Langmuir equation varies as a function of surface coverage, q_e , strictly due to variations in heat of adsorption. The equation is of the form:

$$q_e = K C^{1/n} \quad (5.5)$$

where, K = A constant which is a measure of adsorption capacity.

n = A constant which is a measure of adsorption intensity.

The linearized form of the above:

$$\text{Log } q_e = \text{log } K + \frac{1}{n} \text{log } C \quad (5.6)$$

An attempt was made to fit the data for the observed isotherms in the linearized forms of all the three conventional isotherms described above. The data did not fit satisfactorily in any one of the linearized forms. It seems that the isotherms are of complex nature and do not resemble any of the three isotherms discussed above. Isotherms for NH_4^+ -clay systems at $\text{pH} = 5$ and for PO_4^{3-} -clay systems at $\text{pH} = 7$ are shown in Figures 5.16 & 5.19. Ultimate adsorptive capacities for these systems at all the pH values considered are tabulated in Table VI. The shapes of the adsorption isotherm curves do not

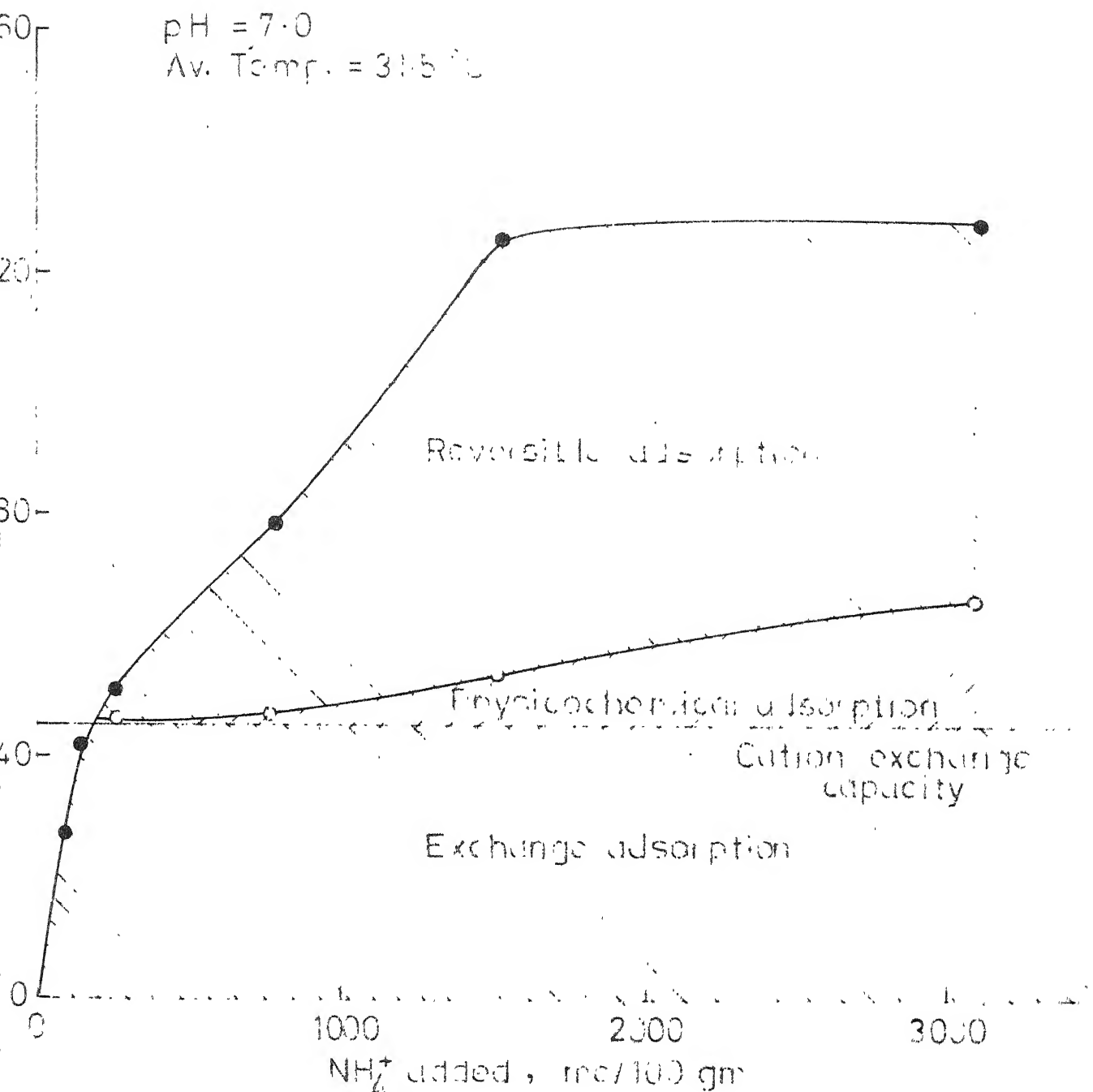


Fig. 5-15 Breakup of total adsorption with NH_4^+ - bentonite system

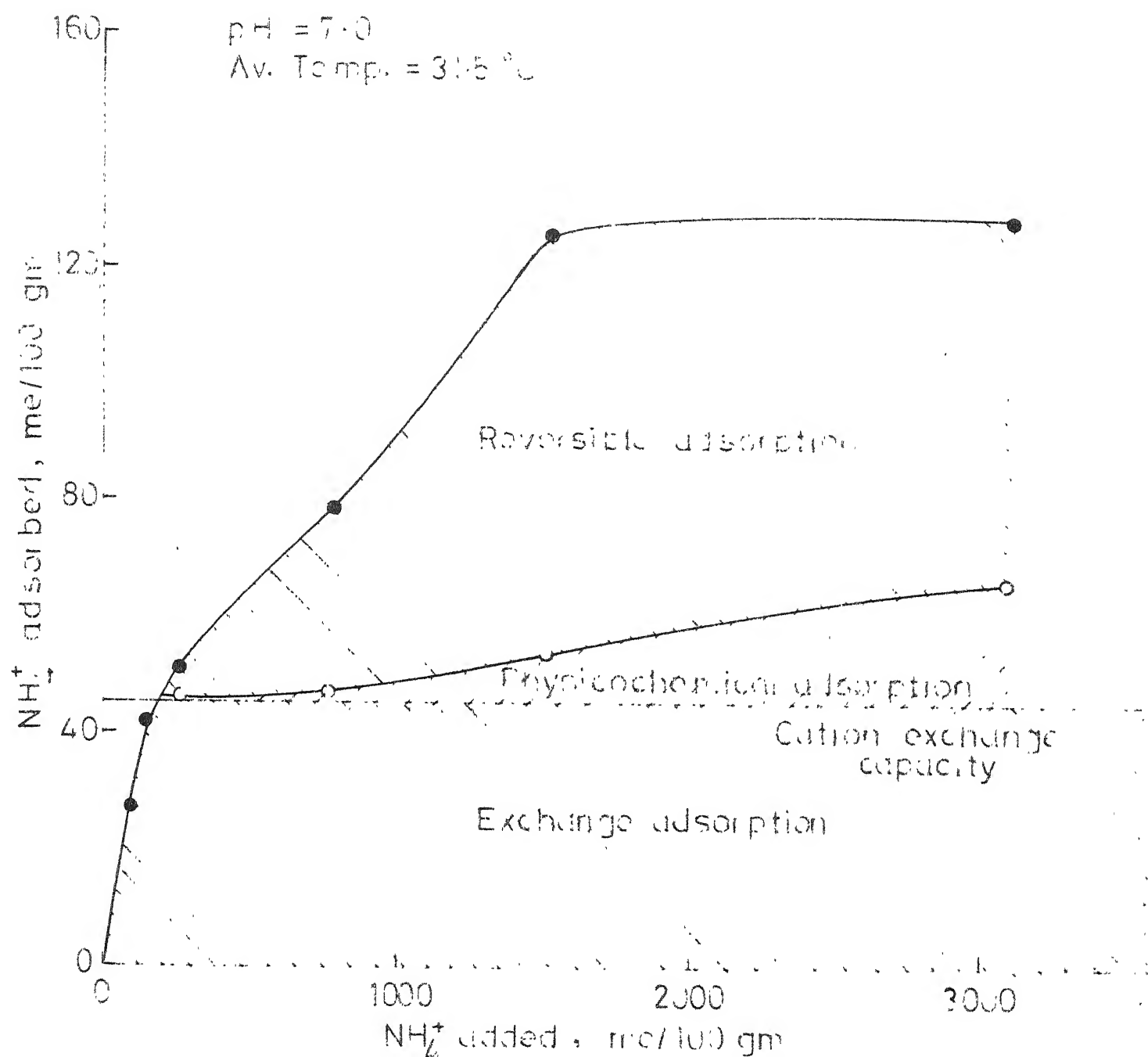


Fig. 5-15 Breakup of total adsorption with NH_4^+ - bentonite system

pH = 7.0

Av. Temp. = 32.0 °C

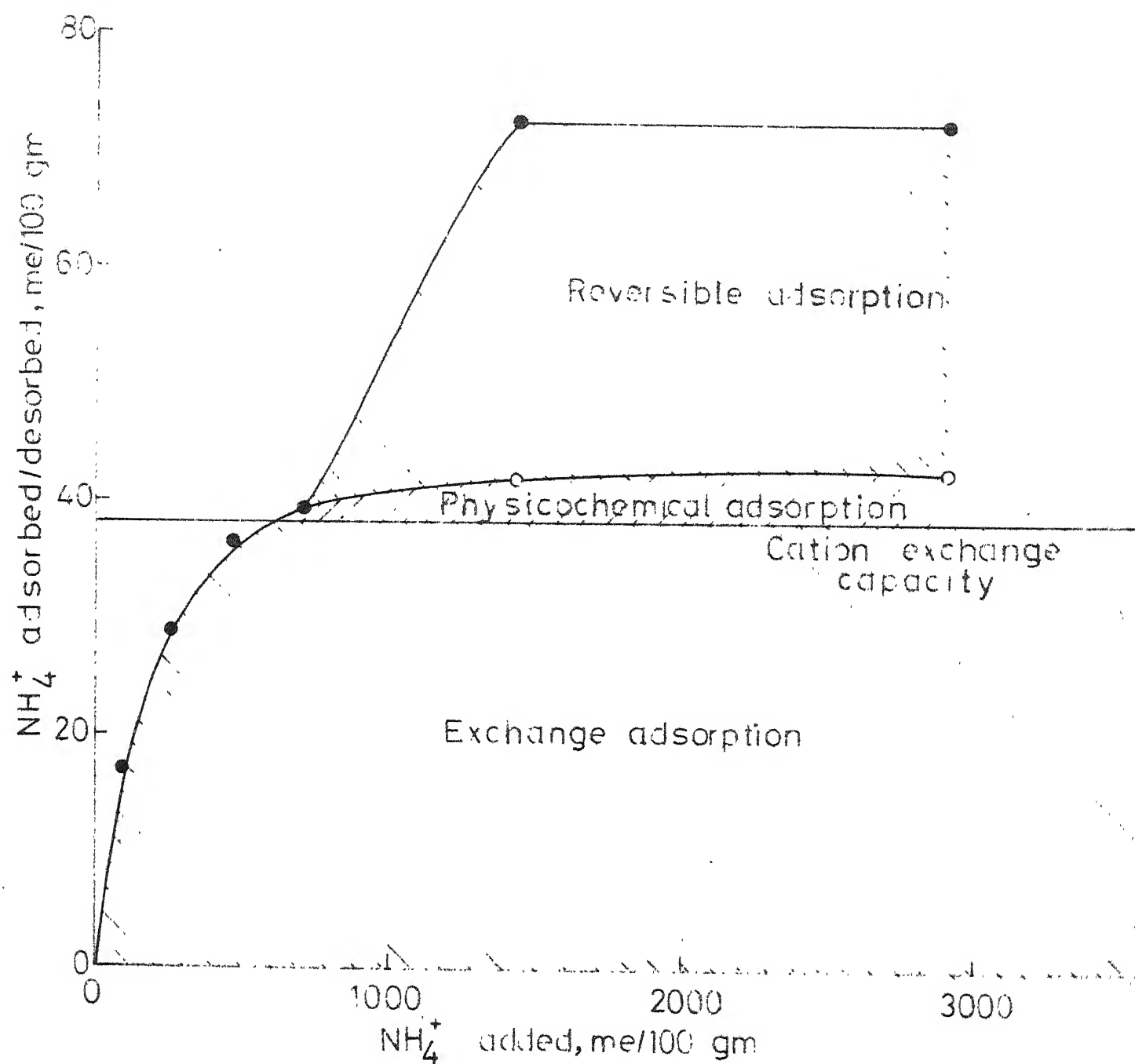


Fig. 5-16 Breakup of total adsorption with NH_4^+ -bauxite system

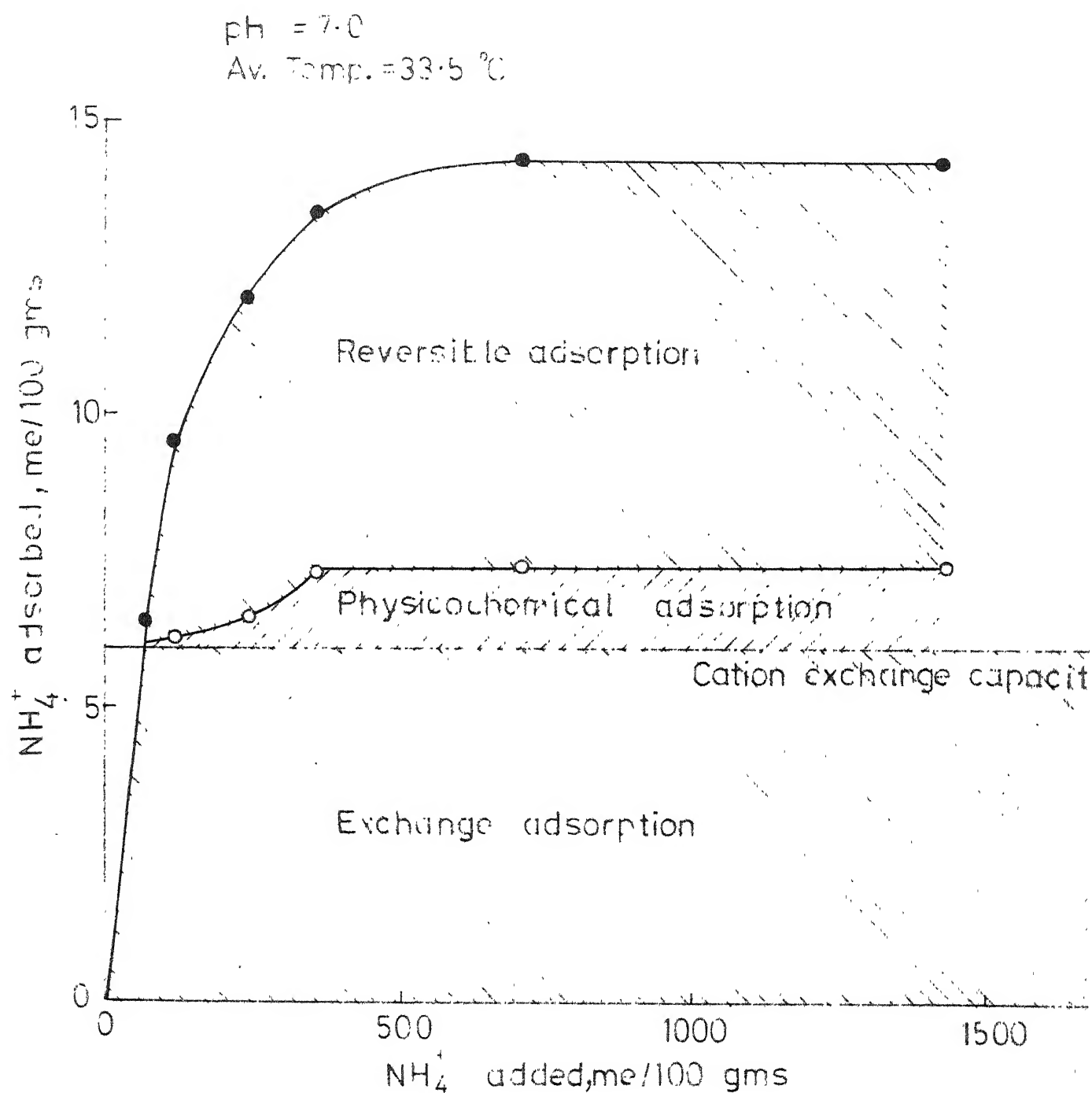


Fig. 5.17 Breakup of total adsorption with NH_4^+ -kaolinite system

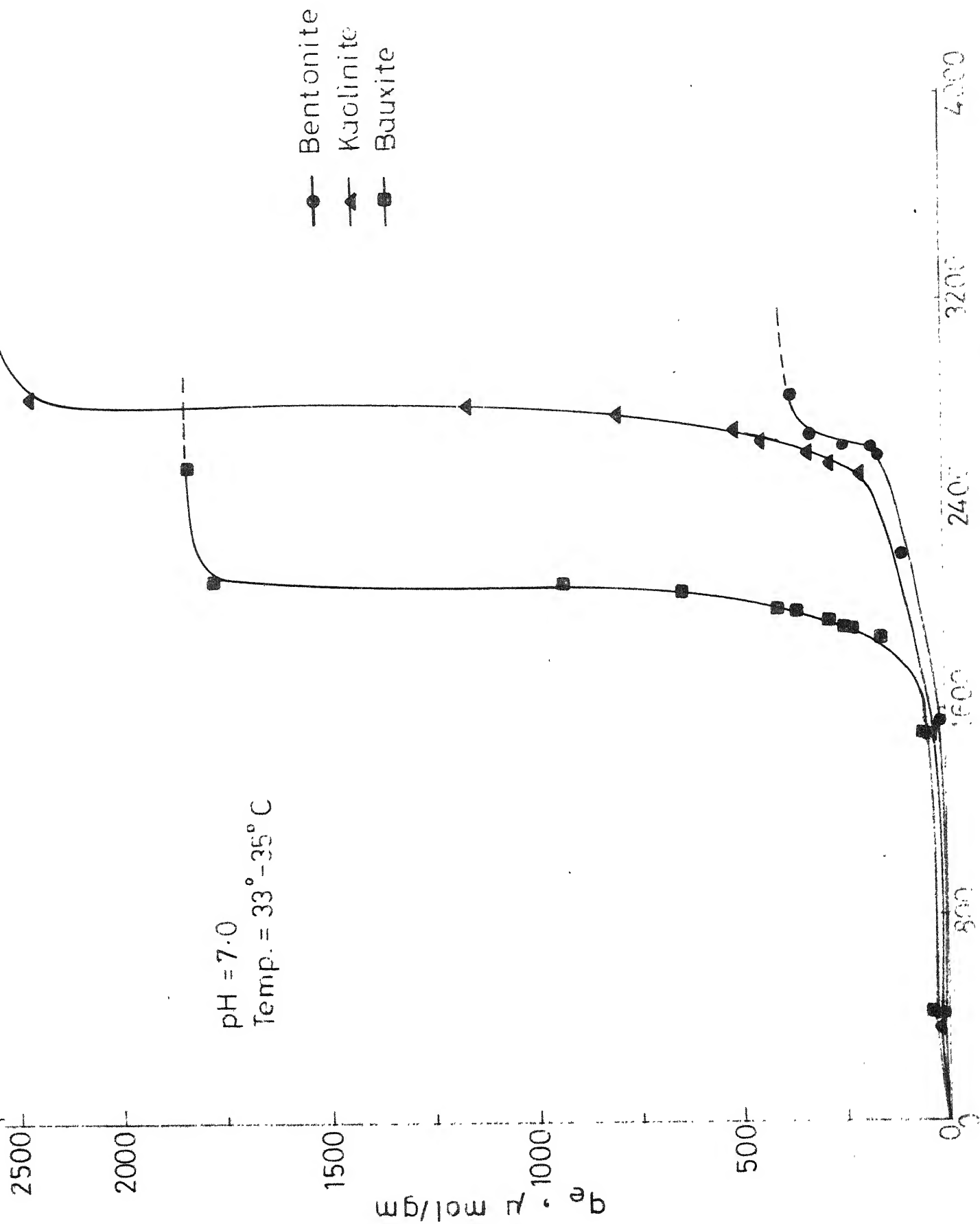


Fig. 1. Adsorption of Cu^{2+} on clay minerals.

300-
200-
100-
0

pH = 5.0
Temp = 28°-32° C

—●— Curve for Tonionite
—▲— " " " " " " " " " " " "
—■— " " " " " " " " " " " "

$q_e, \mu \text{ mol/g}$
200-
100-
0

5 47

700

500

400

300

200

100

Equilibrium concentration, $\mu \text{ mol/l}$

Fig. 5.19 Adsorption of NH_4^+ on clay minerals

resemble any one of the standard shapes given under classification of isotherm in Kipling (1965). However the shapes resemble adsorption isotherms of some ionic detergents on alumina [Kipling (1965)]. Inorganic ions are adsorbed onto the adsorbent by electrostatic attraction. A change in the properties of the solution occurs at the critical micelle concentrations (C.M.C.) which might be formed by the inorganic ions under study. Above this concentration, adsorption characteristics often alter because the concentration of simple ions in solution is reduced and the concentration of new species 'the micelle' with different interfacial behaviour grows. Discontinuities in adsorption are sometimes observed at critical micelle concentrations [Kipling (1965)]. This phenomenon is observed in all the isotherms in Figures 5.15 & 5.16. The isotherms are ^{S-}shaped at low concentrations. This probably corresponds to electrostatic adsorption of one layer followed by adsorption of subsequent layers by van der Waals forces of attraction. [Kipling (1965)]. The difference in behaviour of different clay sorbents has arisen from different polarity of the surfaces. Clay minerals are usually partially polar in nature. On a polar surface, adsorption involves complete attachment of the ionic groups (such as NH_4^+ and PO_4^{3-}) and their micelles. On non-polar surfaces the adsorption would be physical in nature.

From the above discussion in Figures 5.18 & 5.19, the adsorption that is taking place upto inflexion point corresponds to the monolayer variety; but afterwards multilayer adsorption of simple ions along with the formation of their micelles could be taking place.

5.2.6 Calculation of Specific Surface Areas:

Specific surface area is that active fraction of total area as is covered by surface active groups. As mentioned earlier, the data for the observed isotherms do not fit in with the Langmuir, Freundlich or BET's isotherms. However, once the deviations from basic assumptions for these isotherms are appreciated, the best fit for the available data may be used for computations of specific surface area to get a feel of the magnitude of the specific and total surface areas and also the possible mechanism of adsorption. The specific area S_a is given by

$$S_a = Q^0 N_{Av} \sigma^0 \quad (5.7)$$

where

S_a = Specific surface area, m^2/g .

Q^0 = Number of moles of the solute adsorbed per unit weight of the adsorbent in forming a complete monolayer on the surface.

σ^0 = Cross sectional area/molecule.

N_{Av} = Avagadro's number = 6.019×10^{23} .

However as the observed data do not fit in the standard Langmuir form, as such Q^0 cannot be computed. This difficulty has been got around by using the fact that often the values of Q^0 are found to correspond closely to the inflexion point of the q_e versus C plot [Weber (1974)]. The Q^0 values are taken from the adsorption isotherms in Figures 5.18 & 5.19. The specific area is not an inherent property of the sorbent but it varies with the nature of sorbates. The ionic radii and cross sectional areas for NH_3^+ and PO_4^{3-} ions are 1.43 Å, 3.00 Å and 6.4242×10^{-20} and 28.2747×10^{-20} sq m respectively [Nicholhas (1975)]. Table VII gives a comparative statement of the specific areas and total areas. The Q^0 values ^{could also} have been computed from the intercept of the best possible fit of the observed data in Langmuir isotherm model.

As mentioned in Section 5.2.5, the hydrogen ion concentration governs the quantitative distribution of various species of ions from the solutes in aqueous solutions. The quantitative analysis of the various species and their preferential adsorption onto the adsorbent being unknown, the accuracies in the computation of specific surface areas in Table VII could not be improved upon further. However, the limitations of the computations are noted.

From the data in Table VI and the data in the Appendix, it is clear that the adsorptive capacities for NH_4^+ clay system follow the series bentonite > bauxite > kaolinite

Table VII

Total and Specific Surface Areas for Various Adsorption Systems

Clay mineral	pH	Ion adsorbed	Cross sectional area of ion $\text{m}^2 \times 10^{-20}$	Q^0 moles/g $\times 10^{-6}$	q_e moles/g $\times 10^{-6}$	Specific surface area S_a m^2/g	Total surface area S m^2/g	S_a/S $\times 100$, %
Bentonite	5.0	NH_4^+	6.4242	615.00	635.38	23.78	425.61	5.58
Kaolinite	"	"	"	125.00	142.86	4.83	131.91	3.66
Bauxite	"	"	"	530.00	571.40	20.49	56.52	36.25

Bentonite	7.0	PO_4^{3-}	28.4747	362.00	368.42	61.60	425.61	14.47
Kaolinite	"	"	"	710.00	2315.76	120.83	131.91	91.60
Bauxite	"	"	"	250.00	1852.64	42.54	56.52	75.26

and for pH = 7 > for pH = 5 > for pH = 3.0. The bentonite bauxite kaolinite series conforms with the series of the respective cation exchange capacities of these minerals (the C.E.C. values being 45, 38 and 6 me/100 g respectively). Bentonite being a three layered mineral, there is considerable resistance for entry of ions in the intra-lattice space, and hence the comparatively slow initial rate of adsorption but higher ultimate adsorptive capacities compared to kaolinite and bauxite. Increase in hydrogen ion concentrations at low pH values causes competitive adsorption of H^+ ions with NH_4^+ ions and is manifested in the quantitative difference according to the pH series mentioned above.

The adsorptive capacities for PO_4^{3-} -clay systems follow the series kaolinite > bauxite > bentonite. This series is exactly the reverse of the series of the NH_4^+ -clay systems. This observation is consistent with the observation of Fink et al. (1970) where they have found that in general the anion exchange capacities are higher for minerals with lower cation exchange capacities. The pH series for these systems is as follows: adsorption at pH 4 > for pH 7 > for pH = 10. Increased concentration of OH^- ions at higher pH values causes competition with PO_4^{3-} and reduces the adsorptive capacity for PO_4^{3-} . This results in low adsorptive capacities at higher pH values for phosphates.

From the Phase II studies, bauxite comes out to be the natural choice as a potential coagulant aid in Phase III studies, as it has optimum adsorptive capacity for both the ions under consideration, viz. NH_4^+ and PO_4^{3-} . Bentonite has the highest ultimate adsorptive capacity for NH_4^+ adsorption out of the three minerals studied but has low adsorptive capacity for PO_4^{3-} adsorption, whereas kaolinite has the highest PO_4^{3-} adsorptive capacity but has low NH_4^+ adsorptive capacity.

5.3 Phase III Studies:

The objectives of the final phase of the studies have been outlined in Section 3.3. Having obtained information about the adsorption kinetics, nature of adsorption, the rate limiting step(s) in the adsorption and the ultimate adsorptive capacities of the three minerals under different pH conditions, it was decided to check up the magnitudes of removal of NH_4^+ and PO_4^{3-} ions at optimum pH values in coagulation and flocculation process against the removals in Phase II studies, by conducting standard jar tests with alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$) as a representative coagulant. Therefore, Jar Tests were conducted for this purpose.

5.3.1 Jar Tests - Set A:

As can be seen from Table VIII and Figure 5.20(A), an initial NH_4^+ concentration of 107.5 mg/l as N in distilled

Table VIII

Jar Tests - Set A

NH_4^+Cl solution in distilled water

NH_4^+ concentration, 107.50 mg/l as N; Temperature - 36°C, pH - 7.0; Clay concentration - 250 mg/l

Sr. No.	Alum dose mg/l	Bentonite			Kaolinite			Bauxite					
		pH	Turbidity J.T.U.	NH_4^+ mg/l as N remaining $\mu\text{moles/l}$	pH	Turbidity J.T.U.	NH_4^+ mg/l as N remaining $\mu\text{moles/l}$	pH	Turbidity J.T.U.	NH_4^+ mg/l as N remaining $\mu\text{moles/l}$			
1	0.0	4.40	10.00	104.50	7464.28	4.35	100.00	106.50	7607.14	4.35	25.0	102.50	7321.42
2	20.0	4.90	3.70	95.00	6785.71	4.60	12.50	100.00	7142.85	4.70	15.0	97.00	6428.57
3	50.0	4.50	8.25	92.50	5892.85	4.40	6.50	102.00	7285.71	4.50	13.0	96.25	6875.00
4	70.0	4.30	6.00	87.50	6250.00	4.30	7.45	102.50	7321.42	4.40	18.0	97.50	6964.27
5	100.0	4.25	1.50	93.75	6696.42	4.20	8.50	105.00	7500.00	4.10	15.0	98.75	7053.57
6	200.0	4.00	2.25	97.00	6928.57	3.95	5.50	106.25	7589.28	4.05	20.0	98.00	7000.00
7	50.0 (but no minerals added)	6.20	0.60	191.25	7232.14	6.20	0.60	101.25	7232.14	6.20	0.6	101.55	7232.14

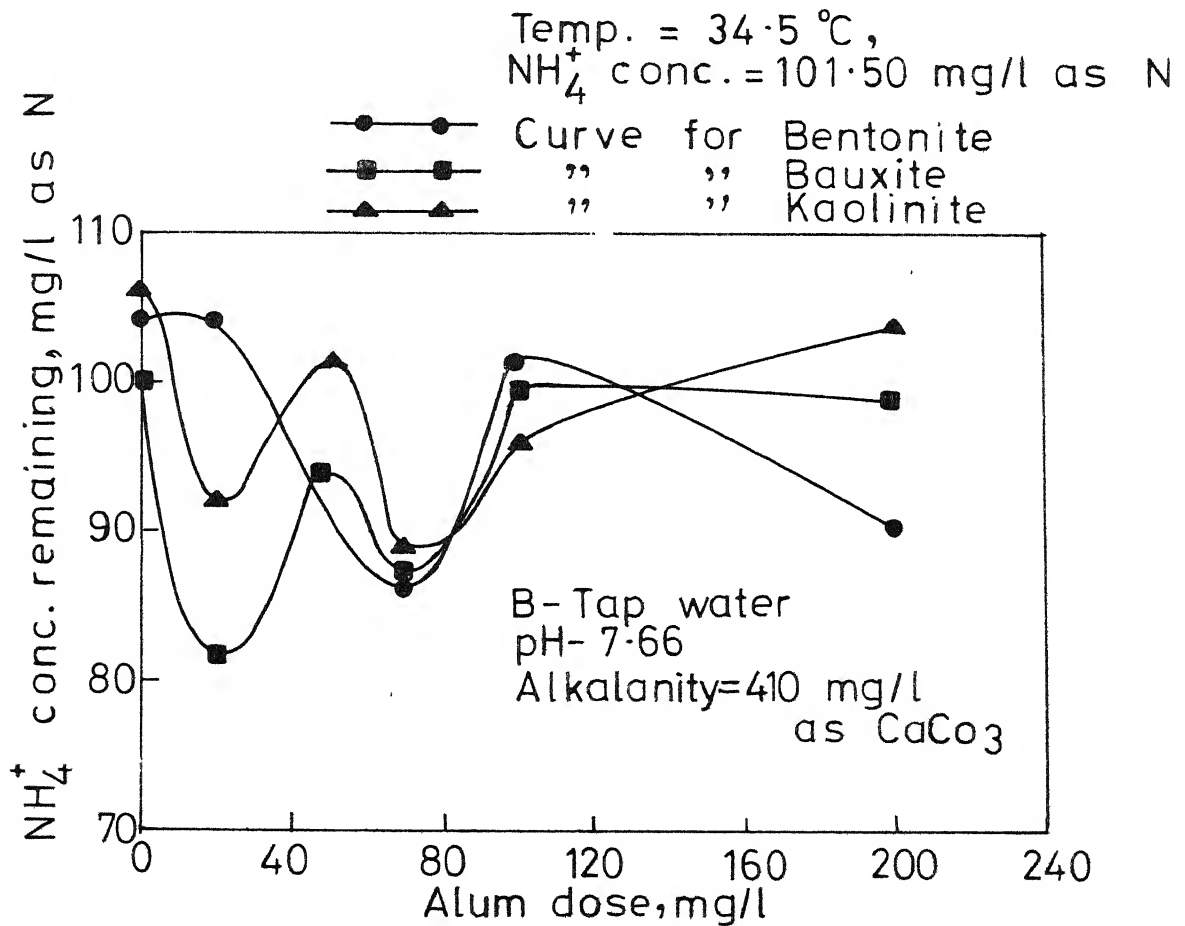
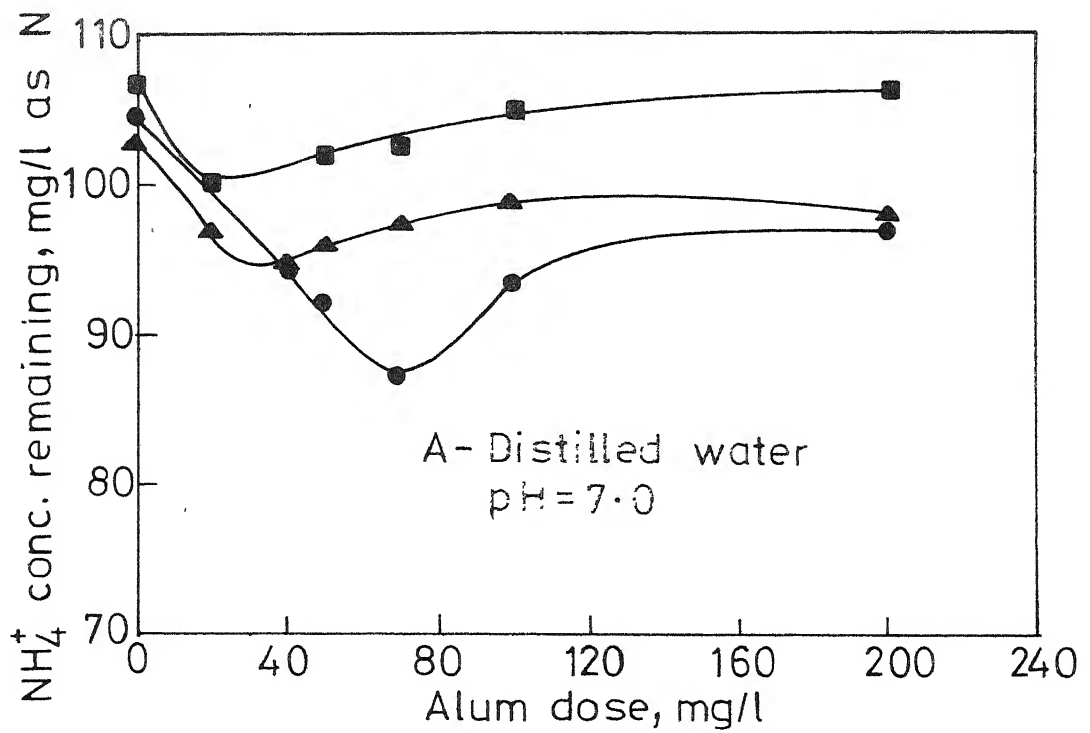


Fig. 5.20 Jar test sets A & B

water was studied for NH_4^+ removal with a clay concentration of 250 mg/l (used in the experiments of ultimate adsorptive capacities) with varying alum dose. The sorbent and the coagulant doses were added to the solute simultaneously. The removal mechanism here essentially consists of adsorption of NH_4^+ ions on clay particles and enmeshment and subsequent settlement of these NH_4^+ -clay complexes subsequently coagulated by alum. For effective coagulation, certain amount of alkalinity which lends the buffering capacity to resist any decrease in pH after alum addition, is necessary. As in this system, no alkalinity is present, the pH is drastically falling on addition of alum as is evident from Table VIII. Coagulation is most effective around the isoelectric point, the pH range being 6 to 7.8 in case of alum coagulation

Weber (1974) . The predominant species in the low pH ranges reached (Table VIII) is Al^{3+} which is a poor coagulant. As a result, the flocculation step is not limiting as sufficient surface has been provided in each case but the destabilization step is limiting because of formation of poorly coagulating species such as Al^{3+} at the low pH values. Though the clay concentrations of all the three minerals were 250 mg/l, the surface areas provided in each case were different, the magnitudes being bentonite > kaolinite > bauxite. From Figure 5.20(A) it is clear that the optimum alum doses for maximum NH_4^+ removal with these minerals also follows this

Jar Tests - Set B

Tap water alkalinity - 410 mg/l as CaCO_3 ; NH_4^+ concentration - 106.25 mg/l as N
Tap water pH - 7.66; Temperature - 36°C

5-57

series. It appears that the amount of alum required to coagulate these NH_4^+ -clay complexes increases with increasing surface areas. This observation is consistent with the normal coagulation process as more alum would be required for adsorption and charge destabilization for more surface areas.

On putting in NH_4^+ -clay solution in the stable Na^+ -clay suspensions, it appears, ^{that the colloids} are destabilized and some NH_4^+ -clay complexes are settling on their own without any alum addition. This phenomenon is more marked in the case of bauxite which is removing as much as 6.42 mg/g NH_4^+ followed by 3.85 mg/g and 1.28 mg/g by bentonite and kaolinite. A comparison of amount of NH_4^+ removed in the batch studies and the present studies indicates that the amount of NH_4^+ removal in jar tests is greater than the ultimate adsorptive capacities in the batch studies. This is clear from Table X.

It appears that alum flocs in addition to enmeshing NH_4^+ -clay complexes, contribute towards additional NH_4^+ removal by offering additional active surface for adsorption. The apparently marginal differences in the removal values in Table X are better appreciated by considering the fact that the contact time for the ultimate adsorptive capacities from batch studies is of the order of 14 to 16 hours whereas that in the case of the coagulation studies is just 51 minutes comprising of the flash mixing (1 min), coagulation (20 min)

Table X

Comparison of NH_4^+ removal in batch studies and in the jar tests

Clay mineral	Removal in distilled water, pH = 7.0		Removal in tap water, pH = 7.66, Alkalinity = 410 mg/l as CaCO_3
	q_e at equilibrium in batch studies mg/g	Maximum NH_4^+ removal in jar test mg/g	Maximum NH_4^+ removal in jar test mg/g
Bentonite	22.82	32.40	25.39
Kaolinite	2.83	9.64	23.46
Bauxite	14.14	14.46	31.82

and settlement time (30 min), the last two steps actually hampering better contact between the solute and sorbent by forming flocs and effectively reducing the effective sorbent surface available for adsorption.

5.3.2 Jar Tests - Set B:

As stated earlier for effective adsorption, certain amount of alkalinity which acts as buffer resisting lowering of pH on alum addition, is necessary [Weber (1974)]. Secondly the coagulation is effective at and around the isoelectric point, the pH range being 6 to 8 for alum coagulation. At or around isoelectric pH, dimeric, ions such as $\text{Al}(\text{OH})^{2+}$ and trimeric ion such as $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and polymeric hydroxometal complexes which are better coagulants than Al^{3+} , dominate the aqueous solution. This results in - - - - -

effective coagulation. So, it was decided to conduct jar tests under similar conditions as in Set A except the fact that tap water which has sufficient alkalinity was used instead of distilled water.

Figure 5.20(B) graphically indicates the results of this set of tests. From Table X, it can be seen that the removal has considerably improved for kaolinite and bauxite but has dropped marginally for bentonite samples, as compared to the removal in Set A tests. Here two conflicting mechanisms are working.

- (1) Effect of alkalinity offering buffering action resisting drop in pH values thereby producing more efficient hydroxo-metal complexes. This mechanism should promote further NH_4^+ removal.
- (2) The Ca^{++} and other cations present in tap water along with its alkalinity are competing with NH_4^+ for adsorption onto the clay mineral surface. This mechanism inhibits NH_4^+ adsorption.

With all other factors remaining constant, the extent of the dominance of the mechanism would finally depend on the characteristics of the active sorbent surface, and apparently the alkalinity effect dominates the Ca^{++} competition in case of kaolinite and bauxite whereas reverse seems to be the case with bentonite.

The curves in Figure 20(A) and (B) more or less follow the pattern of turbidity removal (Tables VIII and IX) as the principal mechanism of NH_4^+ removal is by enmeshment and settlement of NH_4^+ clay complexes by hydroxometal species.

5.3.3 Jar Tests - Set C:

Similar jar tests were performed for S.T.P.P. solutions, their concentrations being the same as in batch studies. But it was found that the soluble phosphates have considerable alum demand. The coagulant first reacts with soluble phosphate species till they are precipitated and then only proceeds to destabilize the colloidal suspension. This is also observed by Weber (1974) and, Ved Prakash and Bokil (1974). For the S.T.P.P. concentrations used, for alum doses of as high as 250 mg/l, no appreciable floc formation was observed. Though analysis of centrifuged samples did show transport of PO_4^{3-} ions onto the clay minerals, as no flocculation and settlement of PO_4^{3-} -clay complexes was observed at these doses, the study was abandoned as any further pursuance would have been for purely theoretical purposes with little practical utility.

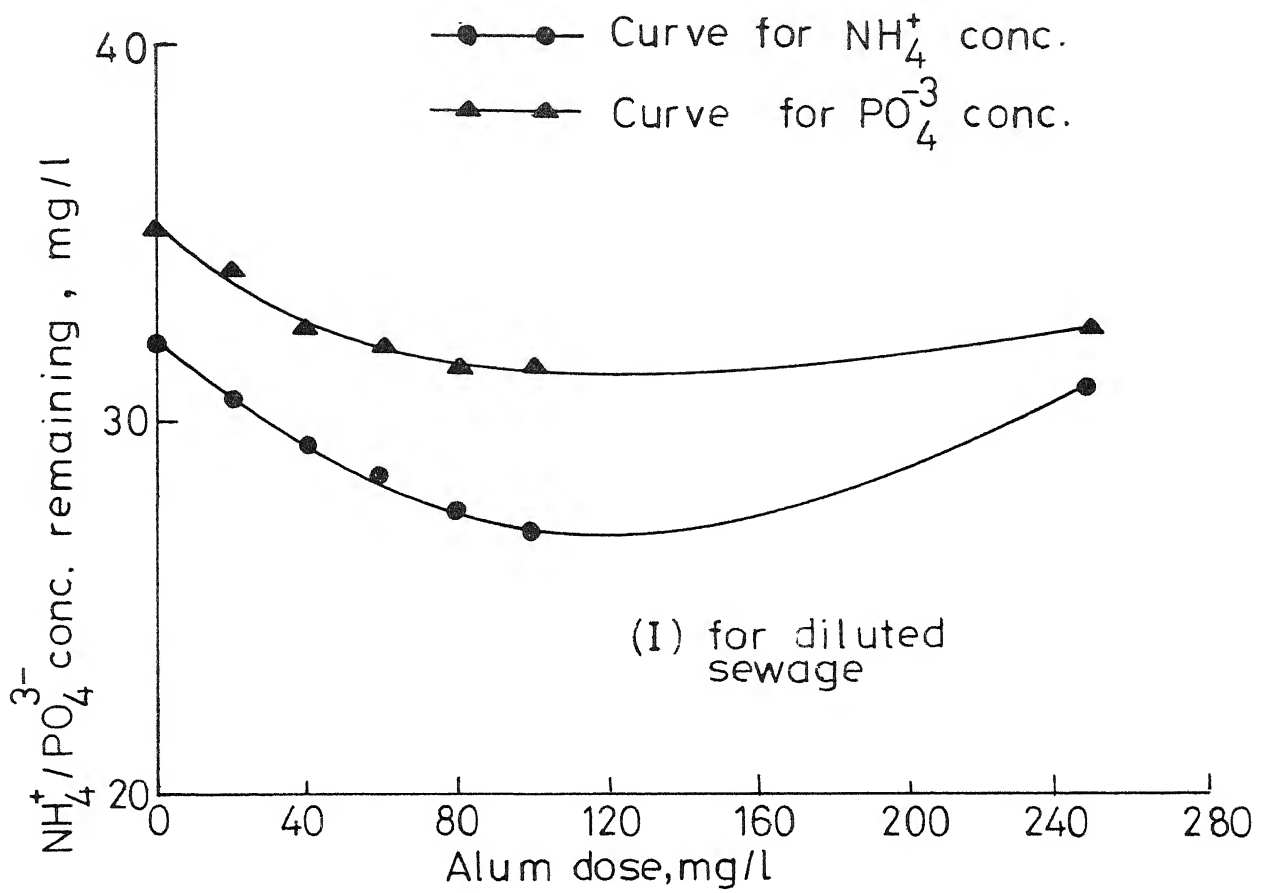
5.3.4 Jar Tests - Set D:

From the batch studies as well as the jar tests A and B, bauxite emerges as the ideal choice (from the minerals considered) with reasonably good ammonium and phosphate

adsorbing capabilities. It was decided to further probe the feasibility of using bauxite as a coagulant aid for a simulated secondary effluent. Herein effect of presence of both NH_4^+ and PO_4^{3-} ions along with other competing ion and also the effect of presence of organics on NH_4^+ and PO_4^{3-} removal in standard jar tests with bauxite as a coagulant aid, was studied. Tap water was used for diluting the domestic ^{raw}/sewage from I.I.T. Kanpur campus to ten percent strength. This was filtered through cotton gauge to eliminate coarser suspended matter but not the finer organics. Common concentrations of NH_4^+ and PO_4^{3-} ions were obtained from literature [Metcalf and Eddy (1978)]. Figure 5.21 and Tables XI and XII illustrate the results of this test.

It can be seen that the optimum alum dose for maximum NH_4^+ and PO_4^{3-} removal for the wastewater without any bauxite addition is of the order of 100 mg/l, which is drastically reduced to about 30 mg/l on addition of 250 mg/l of bauxite. In this test the coagulant aid viz. bauxite was given a contact time of 30 minutes with moderate stirring prior to alum addition.

From Tables XI and XII it can be seen that the amount of NH_4^+ and PO_4^{3-} removed is 11.9 mg/l and 4 mg/l for the given concentrations. This is equivalent to removal of 47.6 mg/g and 16.0 mg/g of bauxite. Compared to the corresponding removals in the batch studies (Table VI) wherein at



NH_4^+ , 5 mg/l as N in tap water
 PO_4^{3-} , 35 mg/l " " " "
 Raw sewage, 10% " " " "

Alkalinity of simulated secondary effluent = 430 mg/lit., as CaCO_3

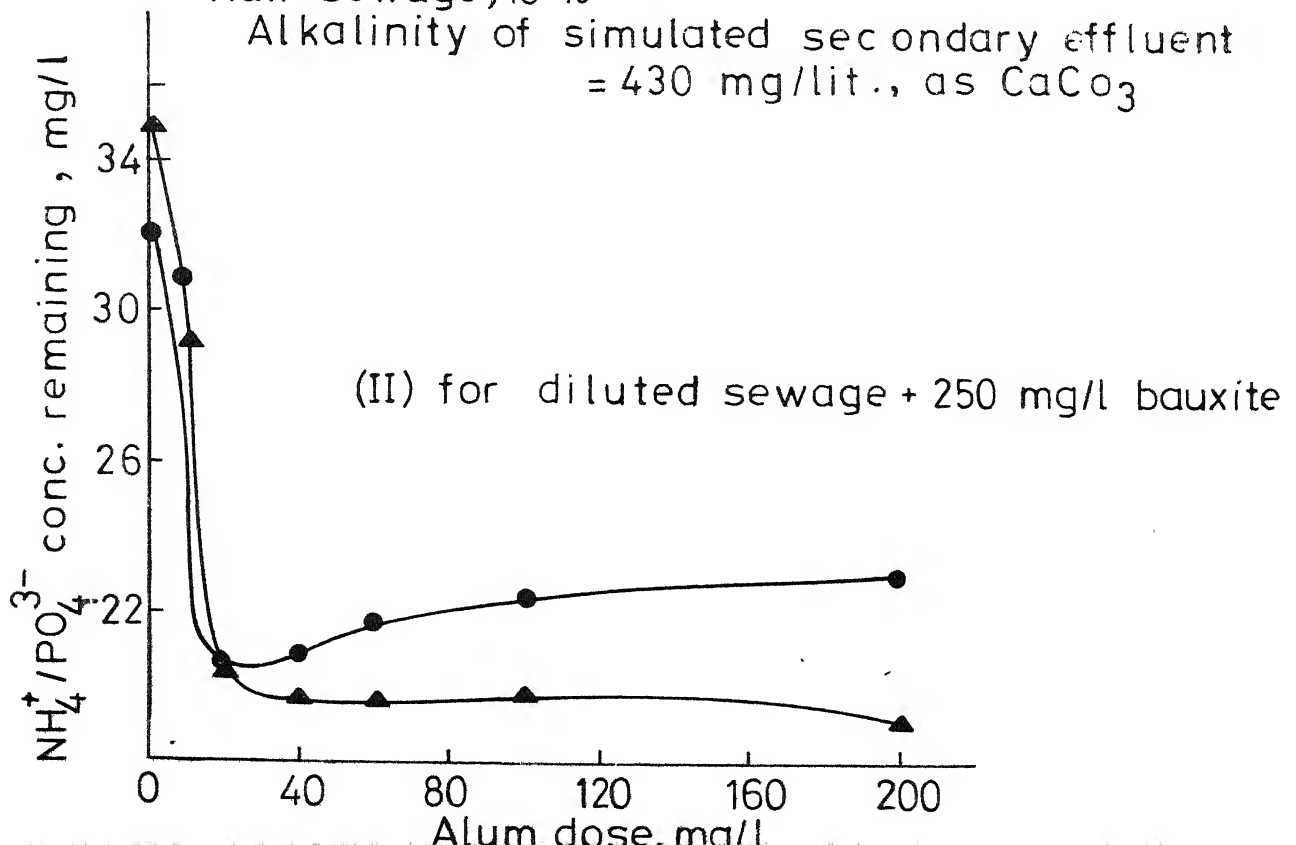


Table XIJar tests - Set D (I)

Diluted sewage, NH_4^+ concentration - 32.14 mg/l; PO_4^{3-} concentration - 35.0 mg/l; pH - 7.23; Temperature - 35.5°C;
Bauxite concentration - 250 mg/l.

Alum dose mg/l	pH	Turbidity J.T.U.	NH ₄ ⁺ remaining		PO ₄ ³⁻ remaining	
			mg/l as N	μmoles/l	mg/l	μmoles/l
0.0	8.29	16.0	32.00	2285.71	35.0	368.42
20.0	8.20	14.0	30.85	2203.57	34.0	357.89
40.0	8.05	12.5	29.60	2114.28	32.5	342.10
60.0	7.95	11.0	28.60	2040.85	32.0	336.84
80.0	7.83	7.8	27.60	1971.42	31.5	331.57
100.0	7.70	11.0	27.00	1928.57	31.0	326.31
200.0	7.23	12.0	30.85	2203.57	32.5	342.10

Table XIIJar Tests - Set D (II)

Diluted sewage, NH_4^+ concentration - 32.14 mg/l;
 PO_4^{3-} concentration - 35.0 mg/l

Alum dose mg/l	pH	Turbidity J.T.U.	NH ₄ ⁺ remaining		PO ₄ ³⁻ remaining	
			mg/l as N	μmoles/l	mg/l	μmoles/l
0.0	8.65	53.0	32.0	2285.71	35.0	368.42
10.0	8.60	37.0	30.6	2185.71	29.0	305.26
20.0	8.50	30.5	20.6	1471.42	20.3	213.68
40.0	8.30	28.0	20.9	1492.85	19.6	206.31
60.0	8.18	18.0	21.6	1542.85	19.6	206.31
100.0	7.83	22.0	22.4	1600.00	19.8	208.42
200.0	7.43	15.0	23.0	1642.85	19.0	200.00

equilibrium, the removal is 14.14 mg/g and 176 mg/g of bauxite. From this it is concluded that the NH_4^+ removal at lower concentrations in a mixed system improves whereas the presence of other competing ions inhibits phosphate adsorption which is clear from the figures stated above.

6. CONCLUSIONS

On the basis of the findings from the present study, following conclusions are drawn:

1. Adsorption of NH_4^+ and PO_4^{3-} onto all the three minerals viz. bentonite, kaolinite and bauxite considered proceeds in two distinct phases. In the first phase, the rate of adsorption is very rapid for about first two hours. This is followed by slow adsorption for another 12 to 14 hours till equilibrium is reached. About 65% to 70% adsorption takes place in the initial rapid adsorption phase.
2. For the pH values considered (3-10), rate and extent of adsorption for NH_4^+ ion is higher at higher pH values and that for PO_4^{3-} ions is lower at higher pH values.
3. The adsorption rate for both the ions is higher for higher ion concentrations.
4. In all the kinetic studies done, intraparticle diffusion (pore diffusion) was found to be the rate limiting step in the first phase of adsorption where, the adsorption was found to be varying almost linearly with $(\text{Time})^{1/2}$. As for the second phase of adsorption 'intraparticle diffusion' only is the rate limiting step for bentonite and kaolinite with regards to NH_4^+ adsorption. For rest of the systems considered, complex mechanism(s) are operative rather than a single one but as such, the

adsorption Vs. $(t)^{1/2}$ data indicates that interparticle diffusion (film diffusion) may be dominating in this phase.

5. Adsorption corresponding to the cation exchange capacity of the minerals is irreversible. A larger fraction of the adsorbed NH_4^+ ions in excess of the cation exchange capacity is readily desorbed. This type of adsorption, therefore, corresponds to physical adsorption. The balance represents irreversible fraction of the physical adsorption which has stayed undesorbed in one washing and may perhaps be chemical adsorption. The rate, extent and equilibrium time for desorption is much less compared to adsorption.
6. The adsorption isotherms do not fit satisfactorily any of the conventional models viz. the Langmuir, Freundlich and the BET. However, the isotherm shapes closely resemble the isotherm for adsorption of some ionic detergents on alumina.
7. For NH_4^+ adsorption the mineral series for favourable adsorption is bentonite > bauxite > kaolinite, the favourable pH series being adsorption at pH = 7 > that at pH = 5 > that at pH = 3. For PO_4^{3-} adsorption, the corresponding mineral series is kaolinite > bauxite > bentonite and adsorption at pH = 4 > at pH = 7 > at pH = 10.
8. Alum coagulation is not desirable for effluents with high phosphate concentration as soluble phosphates have high alum demand.

9. Out of the three minerals studied, bauxite has emerged as the most promising potential coagulent aid having favourable adsorptive capacities with regards to NH_4^+ as well as PO_4^{3-} ions.

7. ENGINEERING SIGNIFICANCE AND SUGGESTIONS FOR FUTURE WORK

7.1 Engineering Significance:

The basic data obtained in the present study is significant both from the point of view of development of suitable low cost coagulant aid as well as development of a suitable soil system for land application for the treatment of nutrient rich wastewaters. Out of the three minerals studied, bauxite has emerged as a promising coagulant aid having reasonably good adsorptive capacities with regard to ammonium and phosphate ions. Soils rich with this minerals such as lateritic soils may be conveniently used as coagulant aids in tertiary wastewater treatment thereby considerably reducing the alum dose.

The observations that the clay minerals can adsorb increasing amounts of ammonium ions over and above their cation exchange capacities and that this excess amount is almost entirely readily desorbed in distilled water lead to some interesting speculations. It is well-known that minerals like montmorillonite (bentonite contains over 80% montmorillonite) and kaolinite form the bulk of the suspended load in rivers and are also main constituents of the bottom sediments. In India, as river courses are invariably used for wastewater disposal by dilution with little pretreatment, the nutrients rich wastewater has ample opportunity to come into contact with

these minerals. With increasing nutrient concentrations, the NH_4^+ and PO_4^{3-} ions are adsorbed by irreversible exchange and chemical adsorption plus by the reversible physical adsorption after the C.E.C. is exceeded. Under normal circumstances these sediments are expected to hold considerable nutrients by physical adsorption, but during floods owing to increased discharge, the sediments are suspended in a more dilute medium hence desorb part of the physically adsorbed ions. This means that the bottom sediments and the suspended load may periodically 'selfpollute' the river water.

The sludge from the tertiary treatment units where those minerals would be used as coagulant aids would be rich in terms of the nutrients and as such, on drying has a potential commercial value as a fertilizer aid and soil conditioner.

7.2 Suggestions for Future Work:

Based on the results of the present study, it is felt that further work should be pursued in the following areas:

1. With the basic data in pure systems for agitated non-flow systems available from this work, column studies may be conducted to ascertain feasibility of using lands rich with lateritic soils as natural sinks for nutrient rich wastewater disposal. It is felt that bauxite holds the key in that it has favourable adsorptive capacities with regards

to NH_4^+ and PO_4^{3-} and also may, in suitable proportion of sand and silt, have good percolation rate compared to kaolinite and a swelling clay mineral like bentonite which are expected to pose clogging problems.

2. Batch & column studies may also be conducted in mixed systems and the effect of competing ions on adsorption onto a heterogeneous mixture of clay minerals (i.e. natural soils) may be quantified.
3. Studies may be conducted to quantify adsorption of organics onto clay minerals.
4. Phase III studies of this work being only exploratory in nature, these studies may be further continued. Varying contact times may be given to the bauxite wastewater system prior to alum addition and the removal be observed. The period of time upto which it is worthwhile to allow contact between the coagulant aid and the influent prior to alum addition may be found out.
5. As the alum doses are very high for phosphate rich influents, jar tests may be conducted with lime as a representative coagulant and the lime doses calculated for influents with varying proportions of the NH_4^+ and PO_4^{3-} ions.

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APPENDIX

Table - A-IInterruption Test Data NH_4^+ -Bentonite System

Bentonite concentration, 5 g/l; pH = 7.0; Temp. = 32.5°C

Sr.No.	Time hrs.	Absorbance	Dilution factor	NH_4^+ conc. mg/l	$U_t = \frac{C_o - C}{C_o - C_e}$
1	0.00	0.328	5	112.50	-
2	0.25	0.311	"	107.00	0.18
3	0.50	0.293	"	101.50	0.36
4	0.75	0.280	"	97.50	0.50
5	1.00	0.271	"	94.50	0.6000

Interruption of 1 hrs.

6	1.25	0.265	"	91.55	0.7083
7	1.50	0.263	"	90.00	0.750
8	1.75	0.252	"	87.50	0.833
9	2.00	0.245	"	86.25	0.875
10	4.00	0.243	"	85.525	0.9100
11	4.25	0.243	"	85.525	0.9100
12	4.50	0.242	"	85.200	0.9125
13	4.75	0.242	"	85.200	0.9125
14	5.00	0.2415	"	85.10	0.9150

Interruption of 1 hr.

15	5.25	0.2415	"	85.10	0.9150
16	5.50	0.2415	"	85.10	0.9150
17	5.75	0.2410	"	85.00	0.9167
18	6.00	0.2405	"	85.00	0.9167
19	8.00	0.2403	"	84.25	0.9416
20	12.00	0.240	"	82.50	1.00

Table - A-II

Adsorption Isotherms NH_4^+ Bentonite System

Temperature - 31.5°C

pH - 7.0

Clay concentration g/l	NH_4^+ as $\text{N}/\text{PO}_4^{3-}$ adsorbed		$C_o - C$ moles/l	q_e moles/g
	mg/l	moles/l		
1	2	3	4	5
0.00	108.75	7763.42	-	-
0.25	104.25	7446.43	316.99	1267.96
0.50	100.00	7138.78	624.64	1249.28
1.00	98.75	7049.54	713.88	713.88
1.50	98.75	7049.54	713.88	475.92
2.50	92.50	6603.36	1160.06	464.02
3.00	88.75	6335.66	1427.76	475.92
4.00	88.00	6282.12	1481.30	370.32
4.50	87.50	6246.43	1516.99	337.11
5.00	80.00	5711.00	2052.42	410.48
7.50	80.00	5711.00	2052.42	263.66

Temperature - 32°C

pH - 5.0

0.00	92.50	6603.40	-	-
0.50	88.00	6285.71	317.69	635.38
1.00	83.75	5976.38	627.02	627.02
1.50	82.50	5889.46	713.94	475.96
2.50	80.00	5711.03	892.37	356.95
3.00	76.25	5443.29	1160.11	386.70
4.00	76.00	5425.44	1177.96	294.49
4.50	73.75	5264.85	1338.55	295.23
5.00	72.50	5175.61	1427.79	285.56
7.50	70.00	4997.11	1606.29	214.17
0.00	15.00	1071.43	-	-
3.00	12.05	860.71	201.72	70.24
0.00	60.00	4285.71	-	-
3.00	54.00	3857.14	428.57	142.86

1	2	3	4	5
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Temperature - 31.5°C

pH - 3.0

0.00	91.00	6500.00	-	-
0.50	86.75	6196.42	303.58	607.16
1.00	82.50	5892.85	607.14	607.14
1.50	80.00	5711.00	789.00	526.00
2.50	77.50	5535.71	924.21	385.71
3.00	76.25	5447.29	1056.71	352.23
4.00	75.00	5357.15	1142.86	285.71
4.50	73.75	5264.85	1231.15	274.47
5.00	72.50	5175.61	1324.39	264.87
7.50	71.25	5089.28	1410.72	188.09

NH₄⁺ Kaolinite System

Temperature - 33.5°C

pH - 7.0

0.00	100.00	7142.85	-	-
0.50	98.90	7064.28	78.57	157.14
1.00	98.00	7000.00	142.85	142.45
2.00	96.25	6875.00	267.85	132.92
3.00	95.00	6785.71	357.14	119.04
6.00	92.00	6571.42	571.43	95.23
10.00	91.00	6500.00	642.85	64.28

Temperature - 33°C

pH - 5

0.00	105.00	7500.00	-	-
0.50	104.00	7428.57	71.43	142.86
1.00	103.00	7357.14	142.86	142.86
2.00	101.50	7250.00	250.00	125.00
3.00	100.80	7200.00	300.00	100.00
6.00	99.50	7107.14	392.86	65.47
10.00	97.50	6964.28	535.72	53.57
0.00	15.00	1071.43	-	-
3.00	14.35	1025.00	46.43	15.48
0.00	60.00	4285.71	-	-
3.00	57.27	4090.71	145.00	65.00

Temperature - 32.5°C

pH - 3.0

0.00	97.50	6964.28	-	-
0.50	97.00	6928.57	35.71	71.42
1.00	96.50	6892.85	71.43	71.43
2.00	95.25	6803.57	160.71	80.35
3.00	94.50	6750.00	214.28	71.42
6.00	94.00	6714.28	250.00	41.67
10.00	93.50	6678.57	285.71	28.57

1	2	3	4	5
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NH_4^+ Bauxite System

Temperature - 33°C

pH - 7.0

0.00	100.00	7142.85	-	-
0.25	97.25	6946.42	196.43	785.72
0.50	94.50	6750.00	392.85	785.70
1.00	93.00	6642.85	500.00	500.00
1.50	91.50	6535.71	607.14	404.76
2.50	87.00	6214.28	928.57	371.43
3.00	84.50	6035.71	1107.14	369.04
4.00	81.00	5785.71	1357.14	339.28
4.50	80.50	5750.00	1392.85	309.52
5.00	78.75	5625.00	1517.85	303.57
7.50	78.75	5625.00	1517.85	202.38

Temperature - 32°C

pH - 5.0

0.00	100.00	7142.85	-	-
0.25	98.00	7000.00	142.85	571.40
0.50	96.25	6875.00	267.85	535.70
1.00	94.00	6714.28	428.57	428.57
1.50	92.25	6589.28	553.57	369.04
2.50	89.75	6410.71	732.14	289.85
3.00	87.00	6214.28	928.57	309.52
4.00	85.00	6071.42	1071.43	267.85
4.50	83.25	5946.42	1196.43	265.87
5.00	82.00	5857.14	1285.74	257.14
7.50	80.00	5714.28	1428.57	190.48
0.00	15.00	1071.43	-	-
3.00	14.35	1025.00	46.43	15.28
0.00	60.00	4285.71	-	-
3.00	56.72	4051.43	234.28	78.93

Temperature - 32.5°C

pH - 3.0

0.00	102.50	7321.42	-	-
0.25	100.75	7198.52	125.00	500.00
0.50	97.25	6982.14	359.28	339.28
1.00	97.00	6928.57	392.85	392.85
1.50	95.00	6785.71	535.71	357.14
2.50	92.50	6607.14	714.28	285.71
3.00	91.00	6500.00	821.42	273.80
4.00	88.75	6339.28	982.14	245.53
4.50	87.00	6214.28	1107.14	246.03
5.00	85.00	6071.42	1250.00	250.00
7.50	84.50	6035.71	1285.71	171.42

1	2	3	4	5
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PO_4^{3-} Bentonite System

Temperature - 33°C

pH - 4.0

0.00	287.50	3026.31	-	-
0.50	265.00	2789.47	236.84	473.68
1.00	255.00	2684.21	342.10	342.10
1.50	250.00	2631.55	394.74	263.16
2.00	247.50	2605.26	421.05	210.52
2.50	245.00	2578.94	447.57	178.94
3.00	240.00	2526.31	500.00	166.67
4.00	220.00	2315.79	710.53	177.63
4.50	210.00	2210.53	815.79	181.28
5.00	205.00	2157.89	868.42	173.89
7.50	192.50	2026.31	1000.00	133.34

Temperature - 33°C

pH - 7.0

0.00	287.50	3026.31	-	-
0.50	270.00	2842.10	184.21	362.42
1.00	255.00	2684.21	342.10	342.10
1.50	252.50	2657.89	368.42	245.61
2.00	250.00	2631.57	394.74	177.37
2.50	247.50	2605.26	421.05	168.47
3.00	245.00	2578.94	447.37	149.12
4.00	230.00	2421.05	605.26	151.31
4.50	220.00	2315.78	710.53	157.89
5.00	215.00	2263.15	763.16	152.63
7.50	210.00	2210.52	815.74	108.77
0.00	50.00	526.31	-	-
5.00	49.05	516.31	21.05	-
0.00	150.00	1578.94	-	-
5.00	148.25	1560.10	18.89	3.72

Temperature - 32.5°C

pH - 10.0

0.00	287.50	3026.31	-	-
0.25	280.00	2947.36	78.94	315.76
0.50	275.00	2894.73	131.57	263.14
1.00	265.00	2789.47	296.83	296.83
1.50	262.50	2763.15	263.15	175.43
2.50	260.00	2736.84	289.47	115.78
3.00	252.50	2665.84	365.41	122.81
4.00	245.00	2578.94	447.36	111.84
4.50	240.00	2576.31	499.99	110.10
5.00	235.00	2473.68	552.62	110.50
7.50	220.00	2315.78	710.52	94.73

1	2	3	4	5
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 PO_4^{3-} Kaolinite System

Temperature - 35°C

pH - 4.0

0.00	375.00	3947.36	-	-
0.25	300.00	3157.89	789.47	3157.88
0.50	243.75	2563.16	1384.20	2768.40
1.00	241.87	2546.25	1401.31	1401.31
1.50	240.00	2526.31	1421.05	947.37
2.50	238.12	2506.57	1440.79	576.32
3.00	236.25	2486.84	1460.52	486.84
4.00	234.37	2467.10	1480.28	370.07
4.50	233.00	2452.63	1494.73	332.16
5.00	232.50	2447.36	1500.00	300.00
7.50	187.50	1973.68	1973.68	263.16

Temperature - 35.5°C

pH - 7.0

0.00	385.00	3947.36	-	-
0.25	320.00	3368.42	578.94	2315.76
0.50	270.00	2842.10	1105.26	2210.52
1.00	265.00	2789.47	1157.89	1157.89
1.50	262.50	2783.16	1184.20	789.46
2.50	258.00	2684.21	1263.15	505.26
3.00	251.25	2644.73	1302.63	434.21
4.00	247.50	2605.26	1342.10	335.52
4.50	245.00	2570.94	1368.42	304.09
5.00	243.75	2565.78	1381.58	276.32
7.50	240.00	2526.31	1421.05	189.47
0.00	50.00	526.31	-	-
5.00	42.85	451.05	75.26	15.05
0.00	150.00	1578.94	-	-
5.00	134.90	1420.00	158.94	31.79

Temperature - 35.5°C

pH - 10.0

0.00	375.00	3947.36	-	-
0.25	360.00	3789.47	157.89	631.56
0.50	350.62	3690.78	256.58	513.16
1.00	337.50	3552.63	394.73	394.73
1.50	330.00	3473.68	473.68	315.79
2.50	310.00	3263.15	684.21	273.68
3.00	300.00	3157.89	789.47	263.16
4.00	277.50	2921.05	1026.31	256.60
4.50	258.50	2721.05	1226.31	272.51
5.00	253.12	2664.47	1282.89	256.58
7.50	250.50	2636.84	1310.52	174.74

1	2	3	4	5
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 PO_4^{3-} Bauxite System

Temperature - 34°C

pH - 4.0

0.00	287.50	3026.31	-	-
0.25	227.50	2394.73	631.58	2526.32
0.50	181.50	1910.52	1115.79	2231.58
1.00	181.00	1905.26	1121.05	1121.05
1.50	179.50	1889.47	1136.84	757.89
2.50	178.00	1873.68	1152.63	461.05
3.00	176.50	1857.89	1168.42	389.47
4.00	175.00	1842.10	1184.21	296.05
4.50	174.00	1831.87	1194.74	265.49
5.00	173.00	1821.05	1205.26	241.05
7.50	172.50	1815.78	1210.53	161.40

Temperature - 33°C

pH - 7.0

0.00	287.50	3026.31	-	-
0.25	243.50	2563.15	463.16	1852.64
0.50	203.50	2142.10	884.21	1768.42
1.00	199.50	2100.00	926.31	926.31
1.50	197.00	2073.68	952.63	635.08
2.50	191.50	2015.78	1010.53	404.21
3.00	188.50	1984.21	1042.10	347.36
4.00	185.50	1952.63	1073.68	268.42
4.50	183.50	1931.57	1094.74	243.27
5.00	182.50	1921.05	1105.26	221.05
7.50	179.50	1889.47	1156.84	151.57
0.00	50.00	526.31	-	-
5.00	44.65	469.91	56.40	11.28
0.00	150.00	1578.94	-	-
5.00	140.00	1473.69	105.25	21.05

Temperature - 35°C

pH - 10.0

0.00	287.50	3026.50	-	-
0.25	277.50	2900.00	126.31	505.24
0.50	267.50	2815.78	210.53	421.06
1.00	257.00	2805.26	321.05	321.05
1.50	251.00	2642.10	3384.21	256.14
2.50	235.00	2473.68	552.63	221.05
3.00	227.00	2389.47	636.89	212.28
4.00	208.50	2194.73	831.58	207.89
4.50	191.50	2015.78	1010.53	224.56
5.00	187.50	1973.68	1052.63	210.52
7.50	185.00	1947.36	1078.95	143.86

Table - A-III

Break up of Total Adsorption for NH_4^+ -Clay Systems NH_4^+ -Bentonite System

Temperature - 33°C

pH - 7.0

Clay concentration g/l	NH_4^+ added me/100 g	NH_4^+ adsorbed		C.E.C. me/100 g	NH_4^+ desorbed me/100 g	NH_4^+ in excess of C.E.C. undesorbed me/100 g &
		me/l	me/100 g			
0.25	3105.37	0.317	126.79	45.00	71.43	10.37
0.50	1552.68	0.625	124.93	"	71.42	8.50
1.00	776.34	0.786	78.57	"	32.14	1.43
1.50	517.56	0.714	47.59	"	2.38	0.21
2.50	310.54	1.160	46.40	"	0.86	0.54
3.00	258.78	1.518	50.59	"	5.36	0.24
4.00	194.08	1.418	35.46	"	-	-
4.50	172.52	1.517	33.71	"	-	-
5.00	155.27	2.053	41.07	"	-	-
7.50	103.57	2.052	27.36	"	-	-

 NH_4^+ -Kaolinite System

Temperature - 32.5°C

pH - 7.0

0.00	-	-	-	-	-	-
0.50	1428.57	0.071	14.29	6.00	7.14	1.44
1.00	714.28	0.143	14.28	"	7.14	1.44
2.00	357.14	0.268	13.39	"	6.25	1.14
3.00	238.09	0.357	11.90	"	5.36	0.55
6.00	119.05	0.571	9.52	"	3.27	0.25
10.00	71.43	0.643	6.43	"	0.36	0.17

 NH_4^+ -Bauxite System

Temperature - 33°C

pH - 7.0

0.00	-	-	-	38.00	-	-
0.25	2928.56	0.143	57.14	"	14.28	4.86
0.50	1464.28	0.359	71.85	"	30.00	3.85
1.00	732.14	0.393	39.28	"	-	1.28
1.50	488.09	0.536	35.71	"	-	-
2.50	292.85	0.714	28.57	"	-	-
3.00	244.04	0.821	27.38	"	-	-
4.00	183.03	0.982	24.55	"	-	-
4.50	162.69	1.107	24.60	"	-	-
5.00	146.42	1.250	25.00	"	-	-
7.50	97.61	1.286	17.14	"	-	-